

Molecular terms, magnetic moments and optical transitions of molecular ions $C_{60}^{m\pm}$

A.V. Nikolaev* and K.H. Michel

Department of Physics, University of Antwerp, UIA, 2610, Antwerpen, Belgium

(Dated: February 1, 2008)

Starting from a multipole expansion of intra-molecular Coulomb interactions, we present configuration interaction calculations of the molecular energy terms of the hole configurations $(h_u^+)^m$, $m = 2 - 5$, of C_{60}^{m+} cations, of the electron configurations t_{1u}^n , $n = 2 - 4$, of the C_{60}^{n-} anions, and of the exciton configurations $(h_u^+ t_{1u}^-)$, $(h_u^+ t_{1g}^-)$ of the neutral C_{60} molecule. The ground state of C_{60}^{2-} is either ${}^3T_{1g}$ or 1A_g , depending on the energy separation between t_{1g} and t_{1u} levels. There are three close (~ 0.03 eV) low lying triplets ${}^3T_{1g}$, 3G_g , ${}^3T_{2g}$ for C_{60}^{2+} , and three quartets ${}^4T_{1u}$, 4G_u , ${}^4T_{2u}$ for C_{60}^{3+} , which can be subjected to the Jahn-Teller effect. The number of low lying nearly degenerate states is largest for $m = 3$ holes. We have calculated the magnetic moments of the hole and electron configurations and found that they are independent of molecular orientation in respect to an external magnetic field. The coupling of spin and orbital momenta differs from the atomic case. We analyze the electronic dipolar transitions $(t_{1u})^2 \rightarrow t_{1u} t_{1g}$ and $(t_{1u})^3 \rightarrow (t_{1u})^2 t_{1g}$ for C_{60}^{2-} and C_{60}^{3-} . Three optical absorption lines (${}^3T_{1g} \rightarrow {}^3H_u$, ${}^3T_{1u}$, 3A_u) are found for the ground level of C_{60}^{2-} and only one line (${}^4A_u \rightarrow {}^4T_{1g}$) for the ground state of C_{60}^{3-} . We compare our results with the experimental data for C_{60}^{n-} in solutions and with earlier theoretical studies.

PACS numbers: 31.10.+z, 31.25.-v, 75.75.+a, 73.21.-b

I. INTRODUCTION

The physics and chemistry of fullerenes is full of surprises. After almost ten years of intensive theoretical and experimental work, unexpected discoveries of ferromagnetic polymerized C_{60} [1] as well as superconductivity in hole doped pristine C_{60} [2] and in lattice-expanded C_{60} [3] raise new questions about the electronic structure of the C_{60} molecule and its molecular ions. Using the field-effect doping techniques, it has been shown that high transition temperatures are achieved for the case of three holes per the C_{60} molecule [2], when many electron effects come into play. Motivated by these new experimental findings, here we present a calculation of the electronic structure of few holes of C_{60}^{m+} . Our second goal is to study the molecular term picture of the C_{60}^{n-} anion ($n = 2, 3, 4$), which behaves as a quasi-element in a vast majority of ionic compounds [4]. When $C_{60}^{m\pm}$ units are in a solid, additional inter-molecular interactions superimposed on the intra-molecular ones should be taken into account and a realistic theory of solids should treat both kinds of interactions on equal footing. Therefore, the consideration of intra-molecular correlations should be a necessary ingredient of a many electron theory aiming to describe superconductivity, magnetic properties or a metal-insulator transition [4, 5, 6, 7, 8]. The problem is also a challenge from experimental point of view [9, 10]. In the present paper we will give quantitative results on the many electron terms and magnetic moments of C_{60}^{m+} and C_{60}^{n-} .

While the one-electronic structure of the neutral C_{60}

molecule is known for many years [11] (in fact, even before the actual discovery of the Buckminsterfullerene [12]) the case of two or three electrons (holes) on the degenerate t_{1u} or h_u shell requires a special treatment. Then the two ($n = 2$) or three ($n = 3$) electrons (holes) are equivalent and should be treated on equal footing. Such kind of situation is very typical for atoms with open electron shells. When an atom has two or more valence electrons on orbitally degenerate states (like p , d or f) its energy spectrum can be very complex reflecting the electronic degrees of freedom. There exist empirical observations known as Hund's rules, which prescribe the occupation of the orbitals, but those are just consequences of the atomic theory of many electron states formulated by Condon and Shortley long ago [13]. The real driving force behind the term splitting is the Coulomb repulsion of the valence electrons. While in atoms electronic energy levels are split due to the multipolar Coulomb intra-atomic interactions, in the case of C_{60} we deal with the intra-molecular ones.

Here we present an approach which was inspired by the theory of many electron atomic states [13]. It is also an extension of our original method of multipole expansion for electronic states [14, 15]. It is worth mentioning that our treatment should not be confused with an ordinary single-determinant Hartree-Fock calculation which does not take into account the intra-molecular correlations and the molecular term structure is overlooked. We will see (Sec. III) that in our approach each basis function represents a Slater determinant, and the solution is found as their linear combination. As such, the method corresponds to a many determinant treatment or configuration interaction (CI). Therefore, the approach is a genuine many electron one as long as we limit ourselves to the relevant orbital space (h_u , t_{1u} or t_{1g}). To our knowledge, in the literature there are only two calculations

*Also at: Institute of Physical Chemistry of RAS, Leninskii prospect 31, 117915, Moscow, Russia

concerning the electronic structure of negatively charged C_{60}^{n-} molecular ions, reported by Negri *et al.* [16], and by Saito *et al.* [17]. In the latter work, however, the assignment of excitations with molecular terms is done only for the neutral molecule ($n = 0$).

In the present paper we assume that the molecule has the icosahedral symmetry. If one wants to consider a distortion of C_{60}^{m+} or C_{60}^{n-} [18, 19, 20, 21, 22], the computed energy levels and their eigenvectors can be used as a starting point for the description of the Jahn-Teller effect in these systems. Indeed, the electron-phonon (or vibronic) coupling occurs if $[\Gamma_{el}]^2$ contains Γ_{vib} [23, 24]. Here Γ_{el} is the symmetry of the electronic molecular term under consideration, while Γ_{vib} is the symmetry of a vibrational normal mode. It is evident then that for a meaningful analysis of the vibrational coupling and the resultant Jahn-Teller distortion, one has to know the symmetry of the corresponding electronic terms, that is the issue of the present study. In addition, now it has been realized that the Jahn-Teller effect for C_{60}^- is rather weak, and the situation is probably best described as dynamic [25], where the molecule on average retains its icosahedral symmetry. The vibronic coupling for C_{60}^{m+} is not so well investigated, but estimated as $\sim 0.1 - 0.2$ eV. We will see that the energy span of the hole configurations a few times exceeds this value. Therefore, if there is a static Jahn-Teller effect for C_{60}^{m+} , it can be treated in the limit of weak or intermediate coupling, leading to a more complex picture where the molecular terms are subjected to further splitting [24, 31].

Since the C_{60} molecule reveals nontrivial degeneracies and peculiarities, its term structure has been studied by group-theoretical methods [26, 27, 28, 29, 30]. The analysis there was focused on the symmetry and number of terms for g^N ($N = 1 - 7$) [26] and h^N ($N = 1 - 9$) [27, 28, 29, 30] configurations, but by itself it can not give a quantitative picture of the splittings. Where our approach overlaps with the group-theoretical one, our findings are in agreement with the latter.

The paper comprises the following sections. First (Sec. II), we introduce the angular dependencies of h_u , t_{1u} and t_{1g} functions. Next (Sec. III), we describe our method of treating multipole Coulomb correlations for many electrons. Then we apply it to hole- and excitonic configurations of the C_{60} molecule, Sec. IV. In Sec. V we give the resultant energy spectra and compare our calculations with those of Negri *et al.* [16] for C_{60}^{2-} . In Sec. VI we compute magnetic moments, in Sec. VII optical lines and line strengths for the electron dipolar transitions of C_{60}^{2-} and C_{60}^{3-} . Finally, we give our conclusions in Sec. VIII.

II. ANGULAR DEPENDENCE OF MOLECULAR ORBITALS

The neutral C_{60} molecule has the highest molecular point group (I_h). Expanding its density in multipole se-

ries one finds that nontrivial angular dependencies are given by the symmetry adapted functions (SAFs) [31] of A_{1g} symmetry with the lowest components characterized by $l = 6$, $l = 10$ and $l = 12$ [32, 33]. That makes the C_{60} fullerene the most spherical molecule among the others. Owing to such unique symmetry, the parentage of π -molecular orbitals in spherical harmonics can be clearly traced [11]. For lowest occupied π -levels of the neutral molecule we have $a_g(l = 0)$, $t_{1u}(l = 1)$, $h_g(l = 2)$, $t_{2u}(l = 3)$, $g_u(l = 3)$, $g_g(l = 4)$, $h_g(l = 4)$ and $h_u(l = 5)$. The corresponding molecular states accommodate 60 electrons and the seven electron shells are completely filled. Then the generalized Unsöld theorem [34] ensures that the resulting electron density of the π -states has full (or unit) icosahedral symmetry A_{1g} . (Here and below we use capital letters for the irreducible representations (irreps) of density and small letters for the irreps of electron wave functions.)

Due to the direct correspondence between these π -shells and the molecular orbital index l , one can immediately find out an orbital part for a given π -state in the same way as we know the orbital parts of s , p , d and f electrons in an atom. Therefore, the type of an irreducible representation (a , t_1 , t_2 , g and h) and the orbital index l uniquely determine the angular dependence of the molecular orbitals. The angular functions are called spherical harmonics adapted for the icosahedral group I_h . Such symmetry adapted functions (SAFs) were tabulated by Cohan in Ref. 32 for all $l \leq 14$. (Unfortunately, Cohan worked with unnormalized spherical harmonics so that it requires some efforts to express SAFs in conventional spherical harmonics Y_l^m .) In particular for the highest occupied molecular orbital (HOMO) $h_u(l = 5)$ one has

$$\psi_1(h_u) = Y_5^{5,s}, \quad (2.1a)$$

$$\psi_2(h_u) = \sqrt{\frac{7}{10}}Y_5^{1,c} + \sqrt{\frac{3}{10}}Y_5^{4,c}, \quad (2.1b)$$

$$\psi_3(h_u) = \sqrt{\frac{7}{10}}Y_5^{1,s} - \sqrt{\frac{3}{10}}Y_5^{4,s}, \quad (2.1c)$$

$$\psi_4(h_u) = \sqrt{\frac{2}{5}}Y_5^{2,c} + \sqrt{\frac{3}{5}}Y_5^{3,c}, \quad (2.1d)$$

$$\psi_5(h_u) = \sqrt{\frac{2}{5}}Y_5^{2,s} - \sqrt{\frac{3}{5}}Y_5^{3,s}. \quad (2.1e)$$

Here the normalized real spherical harmonics are defined with the phase convention of Ref. 31 and the orientation of the C_{60} molecule corresponds to the choice of the z axis as one of 12 fivefold axes and the y axis as one of the twofold axes perpendicular to z [32]. We call this position of C_{60} the orientation of Cohan. In order to transform the molecule to the standard orientation [35] where molecular twofold axes lie along the Cartesian x , y and z direction one has to rotate the molecule anticlockwise about the y axis by an angle $\beta = \arccos(2/\sqrt{10 + 2\sqrt{5}}) \approx 58.28^\circ$ [14]. Each of the h_u orbital function then is expressed in terms of Y_5^τ , where τ stands for $m = 0$ or (m, c) , (m, s)

of real spherical harmonics (Appendix B). In the following we will work with the molecule in the orientation of Cohan. (Of course, the results are independent of the choice of the molecular orientation.)

The lowest unoccupied molecular t_{1u} orbital (LUMO) corresponds to $l = 5$ and has the following three angular components in Cohan's orientation of C_{60} :

$$\psi_1(t_{1u}) = \frac{6}{\sqrt{50}} Y_5^0 + \sqrt{\frac{7}{25}} Y_5^{5,c}, \quad (2.2a)$$

$$\psi_2(t_{1u}) = \sqrt{\frac{3}{10}} Y_5^{1,c} - \sqrt{\frac{7}{10}} Y_5^{4,c}, \quad (2.2b)$$

$$\psi_3(t_{1u}) = \sqrt{\frac{3}{10}} Y_5^{1,s} + \sqrt{\frac{7}{10}} Y_5^{4,s}. \quad (2.2c)$$

The angular parts of t_{1u} LUMO have been derived before in Refs. 36 and 14. In the standard orientation of C_{60} they are given by Table I of Ref. 14. The LUMO-HOMO energy gap is about 2.7 eV [6, 9, 37].

Finally, at an energy about 1.15 eV [9, 38] above LUMO one finds the molecular t_{1g} level with $l = 6$ (LUMO+1). In the orientation of Cohan the angular parts are given by

$$\psi_1(t_{1g}) = Y_6^{5,s}, \quad (2.3a)$$

$$\psi_2(t_{1g}) = \sqrt{\frac{11}{2}} \frac{\sqrt{3}}{5} Y_6^{1,c} - \sqrt{\frac{11}{2}} \frac{1}{5} Y_6^{4,c} + \frac{\sqrt{3}}{5} Y_6^{6,c}, \quad (2.3b)$$

$$\psi_3(t_{1g}) = \sqrt{\frac{11}{2}} \frac{\sqrt{3}}{5} Y_6^{1,s} + \sqrt{\frac{11}{2}} \frac{1}{5} Y_6^{4,s} + \frac{\sqrt{3}}{5} Y_6^{6,s}. \quad (2.3c)$$

III. METHOD OF CALCULATION

Our method of multipole expansion of the Coulomb interaction has been reported before [14, 15]. Here we extend it and apply to the case of the C_{60} molecule with the icosahedral symmetry. In the following we consider in detail the case of two and three t_{1u} electrons. Starting with a pair of electrons we will give a special attention to the procedure of adding one extra t_{1u} electron to the pair. In the same way one can add a fourth electron to the group of three electrons and etc. Therefore, our main goal of treating n electrons can be reached by adding one electron after another.

Since the estimated one-electron spin-orbit coupling is negligible ($\sim 0.16 \text{ cm}^{-1}$) [36], we are working in the “LS (Russell-Saunders)” molecular approximation. (The spin-orbit coupling is a single particle operator and in principle can be included in the calculation [15].) We start with a pair of t_{1u} electrons and label the two-electron basis ket-vectors by a single index I which incorporates a pair of one-electron indices (i_1, i_2) ,

$$|I\rangle = |i_1; i_2\rangle. \quad (3.1)$$

The indices $i = (k, s_z)$ stand for the t_{1u} orbitals ($k = 1, 2, 3$) and the spin projection quantum number. The corresponding basis wave functions are

$$\langle \vec{r}, \vec{r}' | I \rangle = \langle \vec{r} | i_1 \rangle \cdot \langle \vec{r}' | i_2 \rangle, \quad (3.2)$$

where $\langle \vec{r} | i \rangle = \mathcal{R}(r) \langle \hat{n} | i \rangle$. Here \mathcal{R} is the radial component of the t_{1u} molecular orbitals (MO), \hat{n} stands for polar angles $\Omega = (\Theta, \phi)$. There are six orientational t_{1u} vectors (or spin-orbitals) $\langle \hat{n} | i \rangle$ (i.e. $i = 1 - 6$),

$$\langle \hat{n} | i \rangle = \psi_k(\hat{n}) u_s(s_z). \quad (3.3)$$

Here ψ_k are the three t_{1u} MOs as given by Eqs. (2.2a-c) for the Cohan's orientation of C_{60} , u_s is the spin function ($s = \pm$) for the spin projections $s_z = \pm 1/2$ on the z -axis.

The order of indices in (3.1) and (3.2) is important if we associate the first electron with the state i_1 while the second with the state i_2 . From the dynamical equivalence of the electrons we can permute the spin-orbitals of the state $|i_2; i_1\rangle$ to the standard order, Eq. (3.1), by using

$$|i_2; i_1\rangle = -|i_1; i_2\rangle, \quad (3.4)$$

since it requires the interchange of the two electrons. In order to describe the same quantum state we will use the basis vectors (3.1) where $i_1 > i_2$ and apply Eq. (3.4) when needed. (Alternatively, one can use the standard procedure of antisymmetrization of the basis vectors (3.1).) Thus, our basis (3.1) consists of $(6 \times 5)/2 = 15$ different vectors $|I\rangle$.

In the following we will study the intra-molecular correlations of electrons within a formalism based on a multipole expansion of the Coulomb potential between two electrons (charge $e = -1$),

$$V(\vec{r}, \vec{r}') = \frac{1}{|\vec{r} - \vec{r}'|}. \quad (3.5)$$

The multipole expansion in terms of real spherical harmonics Y_l^0 , $Y_l^{m,c}$ and $Y_l^{m,s}$ (we use the phase convention and the definitions of Ref. [31]) reads:

$$V(\vec{r}, \vec{r}') = \sum_{l,\tau} v_l(r, r') Y_l^\tau(\hat{n}) Y_l^\tau(\hat{n}'), \quad (3.6)$$

where τ stands for $m = 0, (m, c)$ or (m, s) of the real spherical harmonics and

$$v_l(r, r') = \left(\frac{r'_<}{r'_>} \right)^l \frac{4\pi}{2l+1}, \quad (3.7)$$

with $r'_> = \max(r, r')$, $r'_< = \min(r, r')$.

The direct matrix elements for the intra-molecular Coulomb interactions are obtained if we consider the $i_1 \rightarrow j_1$ transitions for the first electron and the $i_2 \rightarrow j_2$ transitions for the second (we recall that $i_1 > i_2$ and $j_1 > j_2$). We label this two-electron transition by the index $a_2 = 1$. Starting from Eq. (3.6) we obtain

$$\langle I | V(\vec{r}, \vec{r}') | J \rangle^{Coul} = \sum_{l,\tau} v_l c_{l,\tau}(i_1 j_1) c_{l,\tau}(i_2 j_2), \quad (3.8)$$

where

$$v_l = \int dr r^2 \int dr' r'^2 \mathcal{R}^2(r) \mathcal{R}^2(r') v_l(r, r') \quad (3.9)$$

accounts for the average radial dependence. The transition matrix elements $c_{l,\tau}$ are defined by

$$c_{l,\tau}(ij) = \int d\Omega \langle i|\hat{n}\rangle Y_l^\tau(\hat{n}) \langle \hat{n}|j\rangle. \quad (3.10)$$

The other possibility is to consider the transitions $i_1 \rightarrow j_2$ for the first electron and the transitions $i_2 \rightarrow j_1$ for the second. We label it by the index $a_2 = 2$. This gives the exchange interaction and then we use (3.4) to return to the standard order of the spin-orbitals. We find

$$\langle I|V(\vec{r}, \vec{r}')|J\rangle^{exch} = - \sum_{l,\tau} v_l c_{l,\tau}(i_1 j_2) c_{l,\tau}(i_2 j_1), \quad (3.11)$$

where v_l again is given by Eq. (3.9) and the coefficients $c_{l,\tau}$ by Eq. (3.10). We observe that in the basis with the real t_{1u} orbitals, and with the real spherical harmonics Y_l^τ the coefficients $c_{l,\tau}$ are real.

We start with the spherically symmetric term ($l = 0$) corresponding to the trivial function $Y_0^0 = 1/\sqrt{4\pi}$. The coefficients $c_{l,\tau}$ in (3.10) become diagonal, $c_{l=0}(ij) = 1/\sqrt{4\pi}\delta_{ij}$. In considering the other contributions (with $l > 0$) we take advantage of the selection rules imposed by the coefficients $c_{l,\tau}$, Eq. (3.10). First of all, we notice that the coefficients $c_{l,\tau}$ are diagonal in terms of spin components u_s . Secondly, the odd values of l are excluded due to the parity of the integrand in (3.10), and from the theory of addition of angular momenta we know that $l_{max} = 10$. From these observations we conclude that $l = 0, 2, 4, 6, 8$ and 10 . Earlier the coefficients $c_{l,\tau}$ have been used for the description of the crystal field of C_{60}^- in Ref. [14]. By adding (3.11) to (3.8) we obtain

$$\begin{aligned} \langle I|V(\vec{r}, \vec{r}')|J\rangle &= U_0 \delta(I, J) + v_2 c_2(I|J) + v_4 c_4(I|J) \\ &+ v_6 c_6(I|J) + v_8 c_8(I|J) + v_{10} c_{10}(I|J), \end{aligned} \quad (3.12)$$

where $U_0 = v_0/4\pi$ is the Hubbard repulsion, δ the Kronecker symbol, and

$$\begin{aligned} c_l(I|J) &= \sum_{\tau} [c_{(l,\tau)}(i_1 j_1) c_{(l,\tau)}(i_2 j_2) \\ &- c_{(l,\tau)}(i_1 j_2) c_{(l,\tau)}(i_2 j_1)]. \end{aligned} \quad (3.13)$$

We have studied the secular problem for the 15×15 matrix of intra-molecular interactions and obtained 15 energy levels $E_p[t_{1u}^2]$ ($p = 1 - 15$),

$$\begin{aligned} E_p[t_{1u}^2] &= U_0 + v_2 \lambda_2(p) + v_4 \lambda_4(p) \\ &+ v_6 \lambda_6(p) + v_8 \lambda_8(p) + v_{10} \lambda_{10}(p), \end{aligned} \quad (3.14)$$

where $\lambda_l(p)$ are numerical constants (called “integral” or “molecular invariants” in Refs. [26, 27, 28, 30]). They are quoted in Table I. The 15 levels of (3.14) form three distinct terms, *i.e.* a 9-fold degenerate $\{t_{1u}^2; 1\}$, a 5-fold

TABLE I: Coefficients $\lambda'_l(p) = \lambda_l(p) \times 10^3$ for $(t_{1u})^2$ ($p = 1 - 15$) and $(t_{1u})^3$ ($p' = 1 - 20$).

p	deg.	$l = 2$	4	6	8	10
λ'_l	1-9	(9) -2.943	-21.190	21.817	-39.706	-37.556
	10-14	(5) 0.589	4.238	23.596	7.941	11.641
	15	(1) 5.886	42.379	26.265	79.413	85.436
λ'_l	1-4	(4) -8.829	-63.568	65.450	-119.119	-112.667
	5-14	(10) -3.532	-25.427	68.119	-47.648	-38.872
	15-20	(6) 0.0	0.0	69.898	0.0	10.324

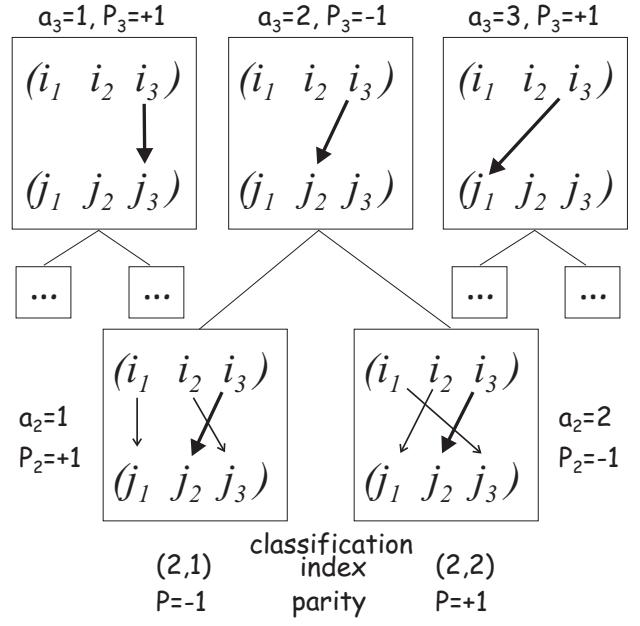


FIG. 1: Diagram for the calculation of a matrix element $\langle i_1 i_2 i_3 | V^{(3)} | j_1 j_2 j_3 \rangle$ by expressing it in terms of different one-electron transitions $i \rightarrow j$. See text for details.

degenerate $\{t_{1u}^2; 2\}$ and a single-level term $\{t_{1u}^2; 3\}$. The symmetry between the four electrons and the two holes within the t_{1u} LUMO configuration implies $\lambda_l(t_{1u}^4; p) = \lambda_l(t_{1u}^2; p)$, $p = 1 - 15$. Therefore, Eq. (3.14) holds also for the case of four t_{1u} electrons if we write $6U_0$ in place of U_0 . In order to study the splitting quantitatively, one has to calculate the radial integrals v_l , Eq. (3.9). We leave this calculation for next section and now move on to the case of three t_{1u} electrons.

For the t_{1u}^3 there are $6 \times 5 \times 4/3! = 20$ basis ket-vectors $|I'\rangle = |i_1 i_2 i_3\rangle$, where $i_1 > i_2 > i_3$. Now for the Coulomb interaction we have a sum of three two-body terms,

$$V^{(3)} = V(\vec{r}_1, \vec{r}_2) + V(\vec{r}_1, \vec{r}_3) + V(\vec{r}_2, \vec{r}_3), \quad (3.15)$$

where each $V(\vec{r}_a, \vec{r}_b)$ is given by the multipole expansion (3.6). In considering a matrix element $\langle I'|V^{(3)}|J'\rangle$ we have many subcases which we also call transitions. We sort them out as shown in Fig. 1. It is important to notice that for the third electron there are only three possibilities, *i.e.* $i_3 \rightarrow j_3$, $i_3 \rightarrow j_2$ and $i_3 \rightarrow j_1$, which

are labeled by $a_3 = 1, 2$ and 3 , respectively. From the anticommutation relations we find that the parity (P_3) of the transitions are $+1, -1$ and $+1$. Each case leaves possibilities for further transitions of the remaining two t_{1u} electrons. We denote their final states as j'_1 and j'_2 . (For $a_3 = 1$ these indices are j_1 and j_2 ; for $a_3 = 2$ j_1 and j_3 , Fig. 1; and for $a_3 = 3$ j_2 and j_3 .) However, the two-electron transitions have been sorted out before when we considered the t_{1u}^2 configuration. In that case there are only two options, ($a_2 = 1$) $i_1 \rightarrow j'_1$, $i_2 \rightarrow j'_2$, and ($a_2 = 2$) $i_1 \rightarrow j'_2$, $i_2 \rightarrow j'_1$. The first has parity $P_2 = +1$, the second $P_2 = -1$.

Therefore, we can classify the transitions by two indices (a_3, a_2) where $a_3 = 1 - 3$ and $a_2 = 1, 2$. For a general case of n electrons it is $(a_n, a_{n-1}, a_{n-2}, \dots, a_2)$, where $a_k = 1, 2, \dots, k$. The parity of an (a_3, a_2) transition is $P = P_3(a_3) P_2(a_2)$, for the general case $P = P_n(a_n) P_{n-1}(a_{n-1}) \dots P_2(a_2)$. The total number of transitions of three t_{1u} electrons is $3 \times 2 = 6$, in general it is $n!$. For each of the subcases we calculate the matrix element of $V^{(3)}$, Eq. (3.15),

$$\begin{aligned} \langle I' | V^{(3)} | J' \rangle^{(a_3, a_2)} &= P_3(a_3) P_2(a_2) \\ &\times \sum_{l, \tau} v_l c_{l, \tau}(i_1 j'_1) c_{l, \tau}(i_2 j'_2) \delta(i_3, j_{a_3}) + p.i. \end{aligned} \quad (3.16)$$

Here *p.i.* stands for the other pair Coulomb interactions $V(\vec{r}_a, \vec{r}_b)$. For three particles there are three terms, Eq. (3.15). The first term is given in Eq. (3.16), two others are found by replacing $c_{l, \tau}(i_1 j'_1) c_{l, \tau}(i_2 j'_2) \delta(i_3, j_{a_3})$ with $c_{l, \tau}(i_1 j'_1) c_{l, \tau}(i_3 j_{a_3}) \delta(i_2, j'_2)$ and with $c_{l, \tau}(i_2 j'_2) c_{l, \tau}(i_3 j_{a_3}) \delta(i_1, j'_1)$. (The parity of the transitions of course remains the same.) For the general case of n electrons one has $\binom{n}{2}$ different pairs for each n -electron transition. (Here $\binom{n}{2}$ is a binomial coefficient.) Finally, the matrix element $\langle I' | V^{(3)} | J' \rangle$ is found as

$$\langle I' | V^{(3)} | J' \rangle = \sum_{a_3=1}^3 \sum_{a_2=1}^2 \langle I' | V^{(3)} | J' \rangle^{(a_3, a_2)}. \quad (3.17)$$

Having found the matrix elements, we solve a 20×20 secular problem for t_{1u}^3 . The energy levels are given by

$$E_{p'}[t_{1u}^3] = \binom{n=3}{2} U_0 + \sum_{l=2}^{10} v_l \lambda_l(p'), \quad (3.18)$$

where only even values of l occur, $p' = 1 - 20$, and λ_l are quoted in Table I. There are three terms, a 4-fold degenerate $\{t_{1u}^3; 1\}$ (ground state), a 10-fold degenerate $\{t_{1u}^3; 2\}$ and a 6-fold degenerate $\{t_{1u}^3; 3\}$, see Table I.

The classification scheme described above is very useful for handling a single-particle interaction \mathcal{A} . In particular, the electron coupling to an external magnetic field, the spin-orbit interaction, crystal electric field effects and the electron dipolar operator fall in this class. The main difference from the Coulomb case is that now the interaction occurs to a single electron (represented by an arrow in Fig. 1) while the rest (the other $(n - 1)$ electrons, or

arrows in Fig. 1) produce $(n - 1)$ Kronecker factors. For example, for the three t_{1u} electrons we have

$$\mathcal{A} = A_1 + A_2 + A_3, \quad (3.19)$$

where A_k refers to a single electron. For each three-electron subcase (a_3, a_2) , Fig. 1, we obtain

$$\begin{aligned} \langle I' | \mathcal{A} | J' \rangle^{(a_3, a_2)} &= P_3(a_3) P_2(a_2) \\ &\times \sum_{l, \tau} \langle i_1 | A_1 | j'_1 \rangle \delta(i_2 j'_2) \delta(i_3, j_{a_3}) + c.p.. \end{aligned} \quad (3.20)$$

c.p. stands for the two other terms obtained from the first by two cyclic permutations, *i.e.* when $i_1 \rightarrow i_2 \rightarrow i_3$ and $j'_1 \rightarrow j'_2 \rightarrow j_{a_3}$. For the general n -electron case there will be n such terms for each matrix element $\langle I' | \mathcal{A} | J' \rangle^{(a_n, a_{n-1}, \dots, a_2)}$.

Finally, we would like to mention that an operator R (rotation or inversion) of the icosahedral group I_h acts on all electrons simultaneously and therefore can be written as $R = R_n R_{n-1} \dots R_1$, where R_k stands for the corresponding one-particle operator. The classification scheme again is useful for determining the matrix elements of the transformation in the many electron space. For example, for three t_{1u} electrons we obtain

$$\langle I | R | J \rangle = \sum_{a_3=1}^3 \sum_{a_2=1}^2 \langle I | R | J \rangle^{(a_3, a_2)}, \quad (3.21)$$

where

$$\langle I | R | J \rangle^{(a_3, a_2)} = P^{(a_3, a_2)} \langle i_1 | R_1 | j'_1 \rangle \langle i_2 | R_2 | j'_2 \rangle \langle i_3 | R_3 | j_{a_3} \rangle.$$

Expressions of that type were used to calculate the characters of molecular terms and to identify their symmetry. The orbital part of the many electron wave function transforms as an irrep of I_h , while the spin function as a single (t_{1u}^2) or double valued (t_{1u}^3) representation of $SO(3)$. Therefore, we classify the molecular terms [26, 27, 28, 29] by the symbol ${}^{2S+1}\Gamma$, where $2S + 1$ is the spin multiplicity and Γ is an irrep of I_h . Thus, the molecular terms are ${}^3T_{1g}$, 1H_g , 1A_g for t_{1u}^2 , and 4A_u , 2H_u , ${}^2T_{1u}$ for t_{1u}^3 , Table I.

IV. APPLICATION TO OTHER CONFIGURATIONS

Below we apply our method for the hole configurations $(h_u^+)^m$ of C_{60}^{m+} and excitonic configurations $h_u^+ t_{1u}^-$, $h_u^+ t_{1g}^-$ of the neutral molecule. We also consider configurations $(t_{1u} t_{1g})$ and $(t_{1u})^2 t_{1g}$, because they are important for calculations of electronic dipolar transitions $(t_{1u})^2 \rightarrow t_{1u} t_{1g}$ and $(t_{1u})^3 \rightarrow (t_{1u})^2 t_{1g}$ of the anions C_{60}^{2-} and C_{60}^{3-} .

A. Hole configurations $(h_u^+)^m$ ($m = 2 - 5$)

The treatment of a m -hole configuration $(h_u^+)^m$ formally coincides [13] with the analogous electronic case

TABLE II: Coefficients $\mu_l(p) \times 10^3$ for $(h_u^+)^2$. The coefficients marked by (*) are not unique depending on integrals v_l , see text for details.

	deg.	$l = 2$	4	6	8	10
${}^3T_{1g}$	(9)	-25.702	-4.238	-8.063	-30.424	-11.151
3G_g	(12)	-18.835	-4.238	-35.345	-2.015	-19.244
${}^3T_{2g}$	(9)	-10.987	-39.553	11.212	-28.746	-11.503
1G_g	(4)	-18.050	0.471	29.597	13.426	11.721
1A_g	(1)	74.162	59.330	57.274	74.228	136.987
* 1H_g	(5)	-18.492	0.471	-12.595	29.970	6.970
* 1H_g	(5)	55.180	16.951	8.429	-18.442	64.255

TABLE III: Coefficients $\mu_l(p) \times 10^3$ for $(h_u^+)^3$. The coefficients marked by (*) are not unique depending on integrals v_l , see text for details.

	deg.	$l = 2$	4	6	8	10
4G_u	(16)	-55.916	-33.903	-61.552	-39.129	-48.232
${}^4T_{1u}$	(12)	-62.783	-33.903	-34.370	-67.538	-40.139
${}^4T_{2u}$	(12)	-48.068	-69.218	-15.095	-65.860	-40.491
${}^2T_{1u} + {}^2T_{2u}$	(12)	-0.392	-5.650	-30.218	-13.676	30.095
${}^2T_{2u}$	(6)	-62.194	-5.650	18.710	-11.293	-3.192
${}^2T_{1u}$	(6)	-47.480	-40.966	37.985	-9.615	-3.544
* 2H_u	(10)	-60.006	-41.550	-43.897	-50.436	-12.533
* 2H_u	(10)	-51.236	-5.650	-24.355	-5.511	-10.208
* 2H_u	(10)	28.220	6.121	-1.637	24.146	61.563
* 2H_u	(10)	45.941	44.376	58.833	54.239	108.509
* 2G_u	(8)	-2.237	-40.966	-36.070	-43.844	38.009
* 2G_u	(8)	38.730	6.121	10.229	-40.794	60.323

$(h_u)^m$, i.e. the Coulomb repulsion between holes and between electrons is the same. The only difference concerns the spherically symmetric term (Hubbard U_0). Below we count the energy from the level of an empty h_u shell. In constructing the basis functions, one should take into account that the one-hole index i_{hu}^+ changes from one to ten, where the five-fold degeneracy is due to the orbital freedom, Eqs. (2.1a-e), and the two-fold degeneracy due to its spin. As a result we obtain the term energies

$$E_p[h_u^{+m}] = \binom{10-m}{2} U_0 + \sum_{l=2}^{10} v_l \mu_l^{(m)}(p), \quad (4.1)$$

where only even values of l occur. The coefficients $\mu_l^{(m)}(p)$ are again molecular invariants. We quote them in Tables II and III for two and three holes, configurations $(h_u^+)^2$ and $(h_u^+)^3$. Some coefficients depend on v_l . This did not occur to t_{1u}^2 or t_{1u}^3 , Table I. These coefficients are marked by star (*) in Tables II and III. For them (μ_l^*) we give values which are calculated with only one parameter v_l . For example, μ_2^* corresponds to the case when $v_{l=2} \neq 0$, while the others are zero, $v_{l \neq 2} = 0$, and etc. Interestingly, the stared terms have off-diagonal matrix elements in the approach of Plakhutin *et al.* (Tables 2 and 3 of Ref. 30). The appearance of μ_l^* implies that the computation of energy splittings, Eq. (4.1), can not

TABLE IV: Coefficients $\nu_l(p) \times 10^3$ for $(h_u^+ t_{1u}^-)$.

	deg.	$l = 2$	4	6	8	10
3H_g	(15)	-6.474	21.189	-0.381	11.652	-23.332
1H_g	(5)	42.967	60.743	17.919	16.694	18.179
3G_g	(12)	-8.240	0.0	11.184	-10.435	19.526
1G_g	(4)	-8.240	14.126	13.725	24.304	103.205
${}^3T_{1g}$	(9)	6.474	-21.189	9.701	-11.652	38.081
${}^1T_{1g}$	(3)	6.474	-21.189	93.578	-11.652	70.528
${}^3T_{2g}$	(9)	15.303	-14.126	-0.678	6.145	11.644
${}^1T_{2g}$	(3)	15.303	-14.126	-0.678	70.660	69.707

be separated in two independent evaluations of v_l and μ_l . Finally, we remark that the “accidental” degeneracy of ${}^2T_{1u}$ and ${}^2T_{2u}$ states of $(h_u)^3$ has been thoroughly studied in Refs. 27, 28, 29, 30.

B. Excitonic configurations $h_u^+ t_{1u}^-$ and $h_u^+ t_{1g}^-$

In order to describe the excitonic configuration $(h_u^+ t_{1u}^-)$ we introduce one h_u hole (missing electron in HOMO) and one t_{1u} electron. The basis functions read

$$|I\rangle = |i_{hu}^+; i_u^-\rangle, \quad (4.2)$$

where now there are 10 states of the h_u hole (index i_{hu}^+) and 6 states of the t_{1u} electron (index i_u^-). The total number of basis functions is 60. The important thing here is that *we have to treat exchange differently*. If we consider I as the initial state and $|J\rangle = |j_{hu}^+; j_u^-\rangle$ as a final state, then *the exchange transition $I \rightarrow J$ is described as two electronic transitions $i_u \rightarrow i_{hu}$ and $j_u \rightarrow j_{hu}$* . For the direct Coulomb interaction we consider $i_u \rightarrow j_u$ and $j_{hu} \rightarrow i_{hu}$. In addition, the sign of the direct Coulomb and exchange interactions has to be reversed [13]. That is,

$$v_l(h_u^+ t_{1u}^-) = -v_l(h_u^- t_{1u}^+), \quad (4.3)$$

for the direct Coulomb (even l) and exchange matrices (even l for $(h_u^+ t_{1u}^-)$ and odd l for $(h_u^+ t_{1g}^-)$). The resulting energy spectrum for both configurations is given by

$$E_p = \Delta\epsilon + \sum_l v_l^{ht} \nu_l(p), \quad (4.4)$$

where $p = 1 - 60$. Here the energy of the closed shell $(h_u)^{10}$ is taken as zero and $\Delta\epsilon$ is an energy associated with the promotion of one electron from the h_u level to the t_{1u} ($\Delta\epsilon = 2.7$ eV [9, 37]) or t_{1g} shell ($\Delta\epsilon = 3.85$ eV [9, 38]) (see also Sec. V). The calculated values of $\nu_l(p)$ are quoted in Table IV for $(h_u^+ t_{1u}^-)$ and in Table V for $(h_u^+ t_{1g}^-)$. The coefficients $\nu_l(p)$ in the Tables correspond to v_l^{ht} with the plus sign, i.e. $v_l^{ht} = v_l > 0$, where v_l are given by Eq. (3.9).

TABLE V: Coefficients $\nu_l(p) \times 10^3$ for $(h_u^+ t_{1g}^-)$.

deg.	$l = 2$	4	6	8	10
3G_u	(12) 21.425	0.0	-19.130	-5.219	18.167
1G_u	(4) 21.425	0.0	-19.130	-5.219	18.167
3H_u	(15) 16.834	-16.204	20.434	4.128	12.320
1H_u	(5) 16.834	-16.204	20.434	4.128	12.320
${}^3T_{1u}$	(9) -16.834	16.204	-14.058	-4.128	-27.802
${}^1T_{1u}$	(3) -16.834	16.204	-14.058	-4.128	-27.802
${}^3T_{2u}$	(9) -39.789	10.802	21.449	4.207	-55.659
${}^1T_{2u}$	(3) -39.789	10.802	21.449	4.207	-55.659
deg.	$l = 1$	3	5	7	9
3G_u	(12) 0.0	0.0	0.0	0.0	0.0
1G_u	(4) 0.0	0.0	0.0	19.382	84.172
3H_u	(15) 0.0	0.0	0.0	0.0	0.0
1H_u	(5) 0.0	0.0	0.0	45.811	3.826
${}^3T_{1u}$	(9) 0.0	0.0	0.0	0.0	0.0
${}^1T_{1u}$	(3) 91.820	0.0	83.877	13.282	0.261
${}^3T_{2u}$	(9) 0.0	0.0	0.0	0.0	0.0
${}^1T_{2u}$	(3) 0.0	142.831	21.746	5.520	0.662
					106.374

TABLE VI: Coefficients $\lambda_l(p) \times 10^3$ for $(t_{1u}t_{1g})$; $\lambda_3 = 0$.

deg.	$l = 2$	4	6	8	10
1A_u	(1) -15.303	-32.407	5.797	-22.605	-15.059
3A_u	(3) -15.303	-32.407	5.797	-22.605	-15.059
3H_u	(15) -1.530	-3.241	14.927	-2.260	-4.757
1H_u	(5) -1.530	-3.241	14.927	-2.260	-4.757
${}^3T_{1u}$	(9) 7.652	16.204	21.014	11.302	2.111
${}^1T_{1u}$	(3) 7.652	16.204	21.014	11.302	2.111
deg.	$l = 1$	5	7	9	11
1A_u	(1) -64.274	41.939	-13.747	31.956	4.127
3A_u	(3) 64.274	-41.939	13.747	-31.956	-4.127
3H_u	(15) -32.137	-4.194	-8.442	-14.152	-23.791
1H_u	(5) 32.137	4.194	8.442	14.152	23.791
${}^3T_{1u}$	(9) -32.137	-20.969	-9.487	-34.238	-41.028
${}^1T_{1u}$	(3) 32.137	20.969	9.487	34.238	41.028

C. $(t_{1u}t_{1g})$ configuration

The basis functions here are

$$|I\rangle = |i_u; i_g\rangle, \quad (4.5)$$

where, as before, the index i_u stands for the t_{1u} LUMO-level ($i_u = 1 - 6$), while the index $i_g = (k, s_z)$ stands for the three t_{1g} (LUMO+1)-orbitals, Eqs. (2.3a-c), and the spin projection s_z . Thus, $i_g = 1 - 6$ and in total, there are $6 \times 6 = 36$ nonequivalent basis vectors $|I\rangle$, Eq. (3.1). From the theory of addition of angular momenta and selection rules we deduce that for the direct Coulomb interactions only the even values $l = 0, 2, 4, 6, 8$ and 10 are relevant, while for exchange these are odd numbers from one to eleven. The calculated $\lambda_l(p)$ are quoted in Table VI.

TABLE VII: Coefficients $\lambda_l(p) \times 10^3$ for $(t_{1u})^2 t_{1g}$; $\lambda_3 = 0$. The coefficients marked by (*) are not unique depending on integrals v_l , see text for details.

	deg.	$l = 2$	4	6	8	10	
4H_g	(20)	-1.413	-17.949	54.714	-37.446	-43.636	
${}^2G_g + {}^2T_{2g}$	(14)	-2.472	-2.244	53.450	3.420	2.127	
${}^4T_{1g}$	(12)	-10.595	-37.393	48.627	-51.009	-50.504	
4A_g	(4)	12.360	11.218	63.844	-17.102	-33.333	
2A_g	(2)	12.360	11.218	63.844	-17.102	-33.333	
*	2H_g	(10)	-1.413	-17.949	54.714	-37.446	-43.636
*	2H_g	(10)	11.301	26.923	62.580	23.765	12.429
*	${}^2T_{1g}$	(6)	-17.976	-30.048	42.958	-12.337	-4.859
*	${}^2T_{1g}$	(6)	13.738	53.979	63.568	83.868	79.472
*	${}^2T_{1g}$	(6)	-1.413	-17.949	54.714	-37.446	-43.636
	deg.	$l = 1$	5	7	9	11	
4H_g	(20)	-64.274	-16.775	-17.407	-38.347	-56.201	
${}^2G_g + {}^2T_{2g}$	(14)	-32.137	-4.194	-8.442	-14.152	-23.791	
${}^4T_{1g}$	(12)	0.0	-41.939	-2.614	-50.216	-43.092	
4A_g	(4)	-64.274	-41.939	-18.975	-68.476	-82.056	
2A_g	(2)	32.137	20.969	9.487	34.238	41.028	
*	2H_g	(10)	-32.137	-21.987	-9.260	-33.523	-39.202
*	2H_g	(10)	32.137	13.599	8.738	23.480	30.584
*	${}^2T_{1g}$	(6)	-64.274	-41.939	-14.929	-33.480	-40.641
*	${}^2T_{1g}$	(6)	-32.137	-17.803	-9.006	-26.724	-18.081
*	${}^2T_{1g}$	(6)	96.411	34.578	22.366	30.075	32.867

D. Three electron configuration $(t_{1u})^2 t_{1g}$

In case of the three-electron $(t_{1u})^2 t_{1g}$ configuration, we construct $(6 \times 5/2) \times 6 = 90$ basis vectors

$$|I'\rangle = |i_{u1} i_{u2} i_g\rangle. \quad (4.6)$$

Here i_{u1} and i_{u2} are indices of the t_{1u} LUMO states, *i.e.* $i_{u1}, i_{u2} = 1 - 6$ and i_g labels six t_{1g} states ($i_g = 1 - 6$). Since in that case we deal with two equivalent t_{1u} electrons, the basis functions are taken with $i_{u1} > i_{u2}$. The calculated λ_l ($p = 1 - 90$) are quoted in Table VII. The important peculiarity of λ_l is that as in the case of few holes, Sec. IV-A, the coefficients marked by star (*) in Table VII (for two 2H_g and three 2T_u terms), exhibit dependence on v_l . For these coefficients (λ_l^*) we give values which are calculated with only one parameter v_l . For example, λ_2^* corresponds to a calculation where $v_{l=2} \neq 0$, $v_{l \neq 2} = 0$ and etc.

Another very interesting observation is that the energy of the 2G_g term “accidentally” coincides with the 2T_g states, Table VII. The same feature has been found for the $t_{1u}(t_{1g})^2$ configuration.

V. ENERGY LEVELS

In order to study the splitting quantitatively we calculated the integrals v_l using three models for radial dependence \mathcal{R} of t_{1u} MOs. In the first model (I) we assume

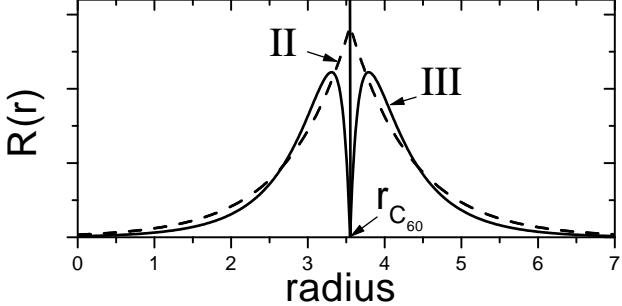


FIG. 2: $|\mathcal{R}(r)|$ for model II (dashed line) and model III (full line) as a function of r (in Å).

TABLE VIII: Calculated v_l for models I, II and III; in eV.

model	$l = 2$	4	6	8	10	12
I	10.195	5.664	3.921	2.998	2.427	2.039
II	6.919	3.064	1.752	1.137	0.797	0.589
III	6.798	2.965	1.673	1.074	0.747	0.550
	$l = 1$	3	5	7	9	11
I	16.991	7.282	4.634	3.398	2.683	2.216
II	13.145	4.390	2.270	1.395	0.944	0.681
III	13.018	4.279	2.181	1.324	0.889	0.637

a delta dependence, *i.e.*

$$\mathcal{R}(r) = \delta(r - r_{C_60})/r^2, \quad (5.1)$$

where $r_{C_60} = 3.55$ Å is the radius of the C₆₀ molecule. This gives

$$v_l = \frac{4\pi}{2l+1} \frac{1}{r_{C_60}}. \quad (5.2)$$

In the second model (II), Fig. 2, we use

$$\mathcal{R}(r) = C \exp(-\sqrt{2|E|}|r - r_{C_60}|), \quad (5.3)$$

where C is determined from the normalization condition and $E = -5.863$ eV, the energy of the carbon p_z atomic orbital in atomic calculations in local density approximation (LDA) (such dependence corresponds to the large distance limit for the carbon p_z -orbital). In the third model (III) we take

$$\mathcal{R}(r) = C' \mathcal{R}_{p_z}(|r - r_{C_60}|), \quad (5.4)$$

where C' is a normalization constant and \mathcal{R}_{p_z} is the radial dependence of the carbon p_z orbital in LDA, Fig. 2. The calculated values of v_l are quoted in Table VIII.

First, from Eqs. (3.14) and (3.18) we calculate the molecular terms of t_{1u}^2 and t_{1u}^3 , Table IX. We observe that despite their differences, models II and III give very close values. Therefore, we believe that the calculated parameters v_l of models II and III are realistic and will change little if a more refined calculation of \mathcal{R} is made. On the other hand, the first model is a rude approximation, and in the following we will not use it. Notice

TABLE IX: Molecular terms and their degeneracies (in parentheses) for $(t_{1u})^2$ and $(t_{1u})^3$ calculated with models I, II and III; in eV. $(^2)U_0$ is zero of energy.

	$(t_{1u})^2$			$(t_{1u})^3$		
	$^3T_{1g}$ (9)	1H_g (5)	1A_g (1)	4A_u (4)	2H_u (10)	$^2T_{1u}$ (6)
I	-0.275	0.175	0.848	-0.824	-0.150	0.299
II	-0.122	0.077	0.375	-0.366	-0.068	0.131
III	-0.117	0.073	0.359	-0.351	-0.066	0.125

TABLE X: Molecular terms of $(t_{1g})^2$ and $(t_{1g})^3$ calculated with models II and III; in eV. $(^2)U_0$ is zero of energy.

	$(t_{1g})^2$			$(t_{1g})^3$		
	$^3T_{1g}$ (9)	1H_g (5)	1A_g (1)	4A_g (4)	2H_g (10)	$^2T_{1g}$ (6)
II	-0.221	0.086	0.547	-0.664	-0.203	0.104
III	-0.215	0.083	0.529	-0.646	-0.199	0.099

that the t_{1u}^2 and t_{1u}^3 energy spectra are the analogue of p^2 (3P , 1D , 1S) and p^3 (4S , 2D , 2P) terms in atomic physics [13]. This occurs because p_x , p_y and p_z orbitals ($Y_1^{1,c}$, $Y_1^{1,s}$ and Y_1^0) also belong to the t_{1u} irrep of I_h [32]. In Table IX as well as in all other Tables of this section (X-XIV) the energy associated with the spherically symmetric multipole component (i.e. $(^2)U_0$ for electrons, $(^{10-m})U_0$ for holes and $\Delta\epsilon$ for excitonic configurations) is put to zero.

Similarly, one can obtain the energy levels of t_{1g}^2 and t_{1g}^3 , Table X. Notice that the energy span of t_{1u}^2 and t_{1u}^3 configurations is almost the same, ~ 0.5 eV, and it is smaller than that of t_{1g}^2 and t_{1g}^3 states, ~ 0.75 eV. However, the zero of energy in Tables IX and X is different for t_{1u}^n and t_{1g}^n configurations. When one t_{1u} electron is promoted to a t_{1g} state, its energy is increased by ~ 1.153 eV [9, 38], that is,

$$\Delta\epsilon_1 = \epsilon(t_{1g}) - \epsilon(t_{1u}) \approx 1.153 \text{ eV}. \quad (5.5)$$

This one-electron energy difference accounts for the interaction of the electron with the carbon nuclei and the “core” like $\sigma-$ and $\pi-$ electrons. Therefore, comparing the energy of $(t_{1g})^2$ with that of $(t_{1u})^2$ states one should add $2\Delta\epsilon_1$ to the $(t_{1g})^2$ values. For the case of three electrons ($(t_{1u})^3$ and $(t_{1g})^3$) we add $3\Delta\epsilon_1$ to the $(t_{1g})^3$ values.

Next, in Tables XI and XII we give results for the hole configurations $(h_u^+)^m$. We observe that the energy span of $(h_u^+)^2$ and $(h_u^+)^3$, ~ 1.2 eV, is almost the same. The magnitude is larger than for electronic t_{1u}^n and t_{1g}^n configurations, Tables IX and X. Even a larger value of energy splitting, ~ 2.4 eV, was obtained for the case of four and five holes, $(h_u^+)^4$ and $(h_u^+)^5$. Another important observation is that the number of states in a small energy interval $\Delta\epsilon \sim 0.03$ eV near the ground state is 30, 40, 25, 6 for $m = 2, 3, 4, 5$, respectively. This suggests that the configuration of $m = 3$ holes is most susceptible

TABLE XI: Molecular terms of $(h_u^+)^2$ and $(h_u^+)^3$ calculated with models II and III; in eV. $(^{10-m})_2 U_0$ is zero of energy.

$(h_u^+)^2$			$(h_u^+)^3$		
deg.	II	III	deg.	II	III
$^3T_{1g}$ (9)	-0.248	-0.242	$^4T_{1u}$ (12)	-0.707	-0.687
3G_g (12)	-0.223	-0.216	4G_u (16)	-0.682	-0.662
$^3T_{2g}$ (9)	-0.219	-0.213	$^4T_{2u}$ (12)	-0.678	-0.658
1G_g (4)	-0.047	-0.049	$^2T_{2u}$ (6)	-0.430	-0.423
1H_g (5)	-0.040	-0.042	2H_u (10)	-0.414	-0.407
1H_g (5)	0.410	0.402	$^2T_{1u}$ (6)	-0.401	-0.394
1A_g (1)	0.989	0.958	2H_u (10)	-0.396	-0.389
			2G_u (8)	-0.077	-0.075
			$^2T_{1u} + ^2T_{2u}$ (12)	-0.065	-0.062
			2H_u (10)	0.156	0.155
			2G_u (8)	0.160	0.159
			2H_u (10)	0.531	0.514

TABLE XII: Molecular terms of $(h_u^+)^4$ and $(h_u^+)^5$ calculated with models II and III; in eV. $(^{10-m})_2 U_0$ is zero of energy.

$(h_u^+)^4$			$(h_u^+)^5$		
deg.	II	III	deg.	II	III
5H_g (25)	-1.377	-1.337	6A_u (6)	-2.294	-2.228
3G_g (12)	-1.005	-0.982	4H_u (20)	-1.716	-1.672
3H_g (15)	-1.004	-0.981	2H_u (10)	-1.324	-1.294
1G_g (4)	-0.819	-0.805	2G_u (8)	-1.323	-1.293
1A_g (1)	-0.814	-0.799	4H_u (20)	-1.265	-1.228
$^3T_{1g}$ (9)	-0.787	-0.767	4G_u (16)	-1.258	-1.221
3G_g (12)	-0.780	-0.760	2A_u (2)	-1.106	-1.079
$^3T_{2g}$ (9)	-0.766	-0.747	2G_u (8)	-1.094	-1.067
1H_g (5)	-0.491	-0.482	$^4T_{2u}$ (12)	-1.086	-1.057
$^1T_{2g}$ (3)	-0.490	-0.481	4G_u (16)	-1.083	-1.054
1H_g (5)	-0.570	-0.460	$^4T_{1u}$ (12)	-1.057	-1.028
$^1T_{1g}$ (3)	-0.461	-0.451	2H_u (10)	-0.816	-0.800
$^3T_{2g}$ (9)	-0.445	-0.430	$^2T_{1u}$ (6)	-0.803	-0.787
3H_g (15)	-0.440	-0.426	2H_u (10)	-0.792	-0.775
$^3T_{1g}$ (9)	-0.434	-0.419	$^2T_{2u}$ (6)	-0.771	-0.755
3H_g (15)	-0.434	-0.419	2H_u (10)	-0.769	-0.748
3G_g (12)	-0.160	-0.157	$^2T_{2u}$ (6)	-0.769	-0.747
$^3T_{2g}$ (9)	-0.160	-0.157	2H_u (10)	-0.747	-0.726
$^3T_{1g}$ (9)	-0.150	-0.148	$^2T_{1u}$ (6)	-0.740	-0.718
1A_g (1)	-0.148	-0.143	$^2T_{1u}$ (6)	-0.487	-0.476
1G_g (4)	-0.138	-0.134	2G_u (8)	-0.453	-0.442
1H_g (5)	0.020	0.014	$^2T_{2u}$ (6)	-0.432	-0.421
1G_g (4)	0.041	0.035	2G_u (8)	-0.417	-0.401
1H_g (5)	0.087	0.089	2A_u (2)	-0.411	-0.395
1G_g (4)	0.090	0.091	2G_u (8)	-0.231	-0.223
1H_g (5)	0.484	0.471	2H_u (10)	-0.227	-0.218
1A_g (1)	1.062	1.027	2H_u (10)	0.144	0.135

for Jahn-Teller distortions of the C₆₀ molecule and hence for hole-phonon coupling which causes superconductivity [2].

The results of calculations of excitonic configurations $(h_u^+ t_{1u}^-)$ and $(h_u^+ t_{1g}^-)$ are quoted in Table XIII. The energy span of $(h_u^+ t_{1g}^-)$, ~ 1.5 eV, greatly exceeds that of $(h_u^+ t_{1u}^-)$, ~ 0.57 eV. A promotion of one electron to the

TABLE XIII: Molecular terms of the excitonic configurations $(h_u^+ t_{1u}^-)$ and $(h_u^+ t_{1g}^-)$ calculated with models II and III; in eV. $\Delta\epsilon$ in Eq. (4.4) is zero of energy.

$(h_u^+ t_{1u}^-)$			$(h_u^+ t_{1g}^-)$		
deg.	II	III	deg.	II	III
3G_g (12)	-0.034	-0.034	$^3T_{2u}$ (9)	-0.244	-0.240
$^3T_{1g}$ (9)	0.014	0.013	$^3T_{1u}$ (9)	-0.118	-0.115
3H_g (15)	0.014	0.013	3H_u (15)	0.117	0.114
$^3T_{2g}$ (9)	0.078	0.076	3G_u (12)	0.123	0.122
1G_g (4)	0.120	0.112	1H_u (5)	0.208	0.200
$^1T_{1g}$ (3)	0.187	0.178	1G_u (4)	0.247	0.238
$^1T_{2g}$ (3)	0.197	0.189	$^1T_{2u}$ (3)	0.513	0.495
1H_g (5)	0.548	0.534	$^1T_{1u}$ (3)	1.341	1.321

TABLE XIV: Molecular terms of $(t_{1u} t_{1g})$ and $(t_{1u})^2 t_{1g}$ calculated with models II and III; in eV. 2G_g and $^2T_{2g}$ are “accidentally” degenerate. $(^n_2)U_0$ is zero of energy.

$(t_{1u} t_{1g})$			$(t_{1u})^2 t_{1g}$		
deg.	II	III	deg.	II	III
1A_u (1)	-0.969	-0.958	4H_g (20)	-1.028	-1.010
3H_u (15)	-0.474	-0.467	$^2T_{1g}$ (6)	-0.991	-0.979
$^3T_{1u}$ (9)	-0.390	-0.384	4A_g (4)	-0.901	-0.886
1H_u (5)	0.473	0.465	$^2G_g + ^2T_{2g}$ (14)	-0.398	-0.395
3A_u (3)	0.503	0.506	$^4T_{1g}$ (12)	-0.376	-0.361
$^1T_{1u}$ (3)	0.697	0.682	2H_g (10)	-0.223	-0.224
			$^2T_{1g}$ (6)	0.004	-0.008
			2H_g (10)	0.449	0.443
			2A_g (2)	0.729	0.714
			$^2T_{1g}$ (6)	1.052	1.045

t_{1u} shell increases the one-electron energy by the factor

$$\Delta\epsilon_2 = \epsilon(t_{1u}) - \epsilon(h_u) \approx 2.69 \text{ eV}. \quad (5.6)$$

The quantity $\Delta\epsilon_2$ is called electron affinity of C₆₀ and it was measured experimentally [9, 37]. It accounts for the energy difference due to the interactions of the electron with the carbon nuclei and the “core” electrons. The value should be taken into account in Eq. (4.4) (i.e. $\Delta\epsilon = \Delta\epsilon_2$) when $(h_u^+ t_{1u}^-)$ is compared with the ground state energy of the neutral molecule. In the case of $(h_u^+ t_{1g}^-)$ one should use $\Delta\epsilon = \Delta\epsilon_1 + \Delta\epsilon_2 = 3.85$ eV in Eq. (4.4).

The molecular terms for $(t_{1u} t_{1g})$ and $(t_{1u})^2 t_{1g}$ are given in Table XIV. The energy span of the excited configurations is relatively large. It is approximately 1.6 eV for $(t_{1u} t_{1g})$ and 2 eV for $(t_{1u})^2 t_{1g}$. Since both configurations imply the excitation of one t_{1u} electron to a t_{1g} state, we should add $\Delta\epsilon_1$ to the energies of the $(t_{1u} t_{1g})$ and $(t_{1u})^2 t_{1g}$ molecular terms, when we compare them with those of the $(t_{1u})^2$ and $(t_{1u})^3$ configurations. The $(t_{1u})^2$ and $(t_{1u} t_{1g})$ (as well as $(t_{1u})^3$ and $(t_{1u})^2 t_{1g}$) groups of terms are of different parity and thus there is no configuration mixing between them. Therefore, although some two-electron molecular terms of the $(t_{1u})^2$ and $(t_{1u} t_{1g})$ configurations overlap, they do not interact with each other. The same holds for the $(t_{1u})^3$ and $(t_{1u})^2 t_{1g}$ con-

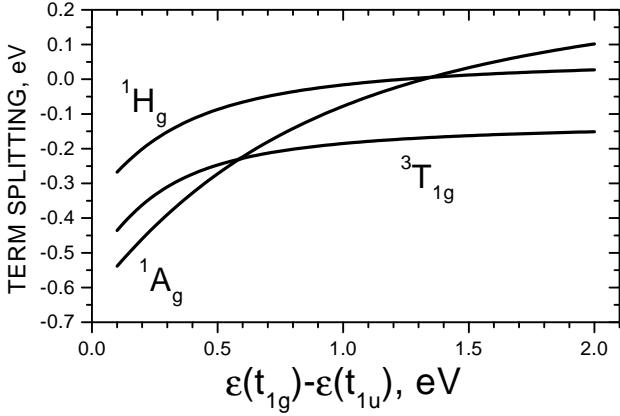


FIG. 3: Three lowest levels of the coupled $(t_{1u})^2 + (t_{1g})^2$ configurations as a function of $\Delta\epsilon_1 = \epsilon(t_{1g}) - \epsilon(t_{1u})$. The ground state is the 1A_g singlet for $\Delta\epsilon_1 < 0.58$ eV, and the ${}^3T_{1g}$ triplet for $\Delta\epsilon_1 > 0.58$ eV.

figurations.

However, there can be a hybridization between terms of the same symmetry of $(t_{1u})^2$ and $(t_{1g})^2$ configurations. The $(t_{1g})^2$ configuration requires promotion of two electrons to the t_{1g} shell, with a subsequent energy increase of $2\Delta\epsilon_1 \sim 2.3$ eV. Since the value is relatively large, the hybridization is expected to be weak. In order to study this issue we have carried out calculations where the mixing between the $(t_{1u})^2$ and $(t_{1g})^2$ configurations was allowed. In the calculation we have considered couplings between two ${}^3T_{1g}$ levels, two 1H_g levels and two 1A_g levels at different values of $\Delta\epsilon_1$. As before, we have employed the method described in Sec. III. We have found that the energy spectrum separates in two groups. A group at lower energies originates from the former $(t_{1u})^2$ levels, while the other group at higher energies has a large parentage of the $(t_{1g})^2$ states. In Fig. 3 we plot the energies of the three lowest levels as a function of $\Delta\epsilon_1$. An interesting feature of Fig. 3 is the crossing of the ${}^3T_{1g}$ triplet with the 1A_g singlet at 0.58 eV with subsequent inversion of their positions. Thus, if $\Delta\epsilon_1 < 0.58$ eV then the ground state is the 1A_g singlet, while for $\Delta\epsilon_1 > 0.58$ eV the ground state is the ${}^3T_{1g}$ triplet. This unusual behavior explains why the 1A_g singlet was reported as the ground state of C_{60}^{2-} by Negri *et al.*, Ref. 16 (QCFF/ π method). From our calculation (Fig. 3) it follows that the reason for this is a small energy difference between t_{1g} and t_{1u} states. In Ref. 16 $\Delta\epsilon_1 = 0.64$ eV, which is only half of the experimental value of 1.153 eV for C_{60}^- [9]. Such low lying t_{1g} states lead to an overestimation of the ${}^1A_g[t_{1u}^2] - {}^1A_g[t_{1g}^2]$ configuration mixing and lowering of the bonding 1A_g term below ${}^3T_{1g}$. The experimental value $\Delta\epsilon_1 = 1.153$ eV [9, 38] implies that the ground state is a triplet, as obtained by our calculations and in accordance with Hund's rules.

VI. MAGNETIC MOMENTS

In this section we will calculate the magnetic moments of $C_{60}^{n\pm}$ for different orientations of the molecule. In a small external magnetic field \vec{H} we add to a many body Coulomb interaction $V(\vec{r}, \vec{r}')$, Eq. (3.6), a magnetic term

$$V_{mag} = -\mathcal{M}_z \cdot H, \quad (6.1)$$

where $\mathcal{M}_z = \sum_{k=1}^n M_z(k)$ is a sum of one-electron (one-hole) terms with

$$\vec{M}(k) = \mu_B(\vec{L}(k) + 2\vec{S}(k)). \quad (6.2)$$

Here μ_B is the Bohr magneton, $k = 1 - n$ for electrons and $k = 1 - m$ for holes. The magnetic moment (6.1) belongs to the class of one-particle operators discussed in Sec. III. Explicitly, for the two-particle case we find

$$\langle I | V_{mag} | J \rangle = [\langle i_1 | M_z | j_1 \rangle \delta(i_2 j_2) + \langle i_2 | M_z | j_2 \rangle \delta(i_1 j_1) - \langle i_1 | M_z | j_2 \rangle \delta(i_2 j_1) - \langle i_2 | M_z | j_1 \rangle \delta(i_1 j_2)] \cdot H, \quad (6.3)$$

where $\langle i | M_z | j \rangle$ stands for the one-particle matrix elements. The generalization of the procedure for a many particle case is given in Sec. III.

The one-particle matrix elements of spin momentum are given by the standard expressions [31, 34]. They are independent of the orientation of the C_{60} molecule. In order to calculate the orbital polarization we start with the C_{60} molecule in the orientation of Cohan [32]. By means of Eqs. (2.2a-c) and taking into account that

$$L_z Y_l^{m,c} = i m Y_l^{m,s}, \quad L_z Y_l^{m,s} = -i m Y_l^{m,c}, \quad (6.4)$$

we obtain for the orbital momentum of t_{1u} states

$$\langle t_{1u}, 2 | L_z | t_{1u}, 3 \rangle = 2.5i, \quad (6.5a)$$

$$\langle t_{1u}, 3 | L_z | t_{1u}, 2 \rangle = -2.5i. \quad (6.5b)$$

The other matrix elements of L_z are zero. (Here and below all values of magnetic moments are given in μ_B .) In the case of h_u states we find

$$\langle h_u, 2 | L_z | h_u, 3 \rangle = \frac{1}{2}i, \quad \langle h_u, 3 | L_z | h_u, 2 \rangle = -\frac{1}{2}i, \quad (6.6a)$$

$$\langle h_u, 4 | L_z | h_u, 5 \rangle = i, \quad \langle h_u, 5 | L_z | h_u, 4 \rangle = -i, \quad (6.6b)$$

and the rest is zero.

There are two equivalent approaches to study the C_{60} molecule in the magnetic field. The first is to use an active operator $R(\omega)$, which rotates the molecule as a three-dimensional object. In such case the magnetic field is always directed along the z -axis, while the position of the molecule is specified by three Euler angles $\omega = (\alpha, \beta, \gamma)$. In the second case the position of the molecule is fixed but the direction of the magnetic field is changed. In the latter case one has to know the matrix components of the three projections of molecular orbital momentum. Below we have adopted the first approach which is more

familiar to us from our previous study of rotator functions [14, 33]. The advantage is that we are working only with the z -component of orbital momentum. The details of the technique are given in Appendices A and B.

Having calculated the matrix elements of V_{mag} as a function of the molecular rotation ω , we diagonalize the matrix $\mathcal{H} = \sum_{a,b} V(\vec{r}_a, \vec{r}_b) + V_{mag}(a)$. The degeneracies of molecular terms are lifted and the magnetic moment of each sublevel p is given by

$$\mathcal{M}(p) = \langle p | \mathcal{M}_z | p \rangle, \quad (6.7)$$

where $|p\rangle$ is the corresponding eigenvector.

For two electrons (or two t_{1u} holes) we obtain $\mathcal{M}_z = (\pm 4.5, \pm 2.5, \pm 2, \pm 0.5, 0)$ for ${}^3T_{1g}$ (ground state), while $\mathcal{M}_z({}^1H_g) = (\pm 5, \pm 2.5, 0)$. In the 1A_g state the spin and the orbital momenta are quenched and $\mathcal{M}_z = 0$. For three electrons we have $\mathcal{M}_z({}^4A_u) = (\pm 3, \pm 1)$ (the ground term); $\mathcal{M}_z({}^2H_u) = (\pm 6, \pm 4, \pm 3.5, \pm 1.5, \pm 1)$ and $\mathcal{M}_z({}^2T_{1u}) = (\pm 3.5, \pm 1.5, \pm 1)$. We immediately conclude that the coupling scheme of orbital and spin momenta is different from the atomic case. In order to clarify this issue we have studied the polarization of spin and orbital momenta separately. By excluding the spin momentum from Eq. (6.2) we have found that $\mathcal{L}_z({}^3T_{1g}) = (\pm 2.5(3), 0(3))$, and $\mathcal{L}_z({}^1H_g) = (\pm 5, \pm 2.5, 0)$ (numbers in parentheses stand for degeneracy). In the molecular term 4A_u the orbital momentum is quenched, $\mathcal{L}_z = 0(4)$, while $\mathcal{L}_z({}^2H_u) = (\pm 5(2), \pm 2.5(2), 0(2))$, and $\mathcal{L}_z({}^2T_{1u}) = (\pm 2.5(2), 0(2))$. By excluding the orbital momentum from Eq. (6.2) we have obtained the results expected from the spin multiplicity index of molecular terms: $2\mathcal{S}_z = (\pm 2(3), 0(3))$ for ${}^3T_{1g}$ (spin triplet state) and $2\mathcal{S}_z = 0(5)$ for 1H_g (spin singlet). For t_{1u}^3 we find $2\mathcal{S}_z({}^4A_u) = (\pm 3, \pm 1)$, $2\mathcal{S}_z({}^2H_u) = \pm 1(5)$, and $2\mathcal{S}_z({}^2T_{1u}) = \pm 1(3)$.

In Sec. V we have already discussed the effect of mixing between the $(t_{1u})^2$ and $(t_{1g})^2$ configurations on the energy of the ground state of the C_{60}^{2-} anion. The hybridization affects also the magnetic moments of the ${}^3T_{1g}$ ground state, which are given by

$$\mathcal{M} = 0, \pm g, \pm 2, \pm(2+g), \pm(4+g). \quad (6.8)$$

The magnetic moments of the unhybridized ${}^3T_{1g}$ triplet of the pristine t_{1u}^2 configuration correspond to $g = 0.5$ (dashed line in Fig. 4). The evolution of the g -factor as a function of $\Delta\epsilon_1$ is given in Fig. 4.

The results for the hole configurations $(h_u^+)^m$ are quoted in Tables XV-XVIII. In the case of four or five holes the number of molecular terms is too big (27) and we give only magnetic moments for ten lowest states. In general, magnetic moments are described by an expression of the type (6.8) although in some cases two distinct values of g are required.

Interestingly, we have found that the calculated magnetic moments are independent of the molecular orientation. The conclusion holds for both t_{1u} and h_u shells and we think that there must be a hidden group-theoretical

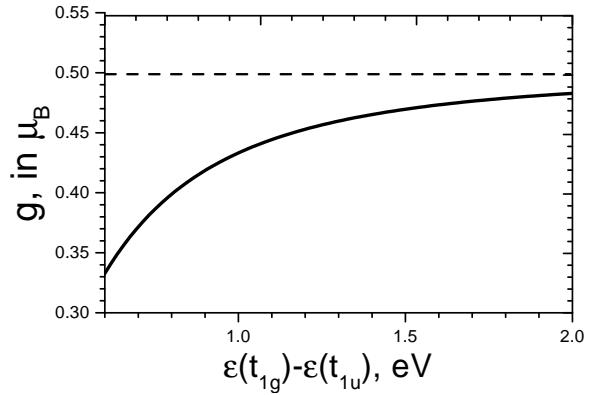


FIG. 4: g for the ground state triplet ${}^3T_{1g}$ as a function of $\Delta\epsilon_1$, C_{60}^{2-} . The corresponding magnetic moments are given by Eq. (6.8).

TABLE XV: The magnetic moments \mathcal{M} and the orbital momenta \mathcal{L} of $(h_u^+)^2$, in μ_B .

	\mathcal{M}	g	\mathcal{L}
${}^3T_{1g}$	$0; \pm(1, 3, 4, 5)g$	0.5	$0, 0, 0, \pm(1, 1, 1)g$
3G_g	$\pm(1, 1, 3, 3, 5, 5)g$	0.5	$\pm(1, 1, 1, 1, 1, 1)g$
${}^3T_{2g}$	$0, 0, 0, \pm(1, 1, 1)g$	2	$0(9)$
1G_g	$\pm(1, 1)g$	0.8333	\mathcal{M}
1H_g	$0; \pm(1, 2)g$	0.0668	\mathcal{M}
1H_g	$0; \pm(1, 2)g$	0.2335	\mathcal{M}
1A_g	0	0	0

reason behind this. We consider the result as unexpected, because the magnetic moment of a π or δ MO of diatomic molecules is anisotropic in respect to the direction of the magnetic field. From our previous study of C_{60}^- in a cubic environment it also follows that the crystal field of C_{60}^- exhibits strong dependence on its orientation [14]. In case of the C_{60} molecule, the orbital t_{1u} (or h_u) space of the icosahedral symmetry is greatly reduced in comparison with the 11 dimensional $l = 5$ space of the rotation

TABLE XVI: Magnetic moments \mathcal{M} of $(h_u^+)^3$, in μ_B . ${}^2T_{1u}$ and ${}^2T_{2u}$ states are degenerate.

	\mathcal{M}	g
${}^4T_{1u}$	$\pm(1, 2, 3, 5, 6, 7)g$	0.5
4G_u	$\pm(1, 1, 3, 3, 5, 5, 7, 7)g$	0.5
${}^4T_{2u}$	$\pm(1, 1, 1, 3, 3, 3)g$	1.0
${}^2T_{2u}$	$\pm(1, 1, 1)g$	1.0
2H_u	$\pm(g_1, g_2, 1, 2 - g_2, 2 - g_1)$	0.6529, 0.8265
${}^2T_{1u}$	$\pm(g, 1, 2 - g)$	0.25
2H_u	$\pm(g_1, g_2, 1, 2 - g_2, 2 + g_1)$	0.2218, 0.3891
2G_u	$\pm(g, g, 2 - g, 2 - g)$	0.8983
${}^2T_{1u} + {}^2T_{2u}$	$\pm(1, 1, 1, 1, 1)g$	1
2H_u	$\pm(g_1, g_2, 1, 2 - g_2, 2 - g_1)$	0.9578, 0.9789
2G_u	$\pm(g, g, 2 - g, 2 - g)$	0.5650
2H_u	$\pm(0, 1, 2, 3, 4)g$	0.5

TABLE XVII: Magnetic moments \mathcal{M} for ten lowest molecular terms of $(h_u^+)^4$, in μ_B .

\mathcal{M}	g
5H_g	$0, \pm(1, 2, 2, 3, 4, 5, 6, 6, 7, 8, 9, 10) g$
3G_g	0.5
3G_g	$\pm(g, g, 2 - g, 2 - g, 2 + g, 2 + g)$
3H_g	0.310
3H_g	$0, \pm(g_1, g_2, 2 - g_2, 2 - g_1, 2, 2 + g_1, 2 + g_2)$
1G_g	$0.046, 0.092$
1G_g	$\pm(1, 1) g$
1A_g	0.011
1A_g	0
${}^3T_{1g}$	$0, \pm(g, 2 - g, 2, 2 + g)$
3G_g	0.052
3G_g	$\pm(g, g, 2 - g, 2 - g, 2 + g, 2 + g)$
${}^3T_{2g}$	0.023
${}^3T_{2g}$	$0, 0, 0, \pm(1, 1, 1) g$
1H_g	2.0
1H_g	$0, \pm(1, 2) g$
${}^1T_{2g}$	0.146
${}^1T_{2g}$	$0, 0, 0$

TABLE XVIII: Magnetic moments \mathcal{M} for ten lowest molecular terms of $(h_u^+)^5$, in μ_B . $\mathcal{M}({}^4H)$ stands for $\pm(g_1, g_2, 1, 2 - g_2, 2 - g_1, 2 + g_1, 2 + g_2, 3, 4 - g_2, 4 - g_1)$.

\mathcal{M}	g
6A_u	$\pm(1, 3, 5) g$
4H_u	$\mathcal{M}({}^4H)$
2H_u	$0.533, 0.766$
2H_u	$\pm(g_1, g_2, 1, 2 - g_2, 2 - g_1)$
2G_u	$0.873, 0.936$
2G_u	$\pm(g, g, 2 - g, 2 - g)$
4H_u	0.366
4H_u	$\mathcal{M}({}^4H)$
4G_u	$0.866, 0.933$
4G_u	$\pm(g, g, 2 - g, 2 - g, 2 + g, 2 + g, 4 - g, 4 - g)$
2A_u	0.167
2A_u	$\pm g$
2G_u	1.0
2G_u	$\pm(g, g, 2 - g, 2 - g)$
${}^4T_{2u}$	0.978
${}^4T_{2u}$	$\pm(1, 1, 1, 3, 3, 3) g$
4G_u	1.0
4G_u	$\pm(g, g, 2 - g, 2 - g, 2 + g, 2 + g, 4 - g, 4 - g)$
4G_u	0.5

group $SO(3)$. However, this is not accompanied by an anisotropic behavior of orbital momenta.

In order to understand this issue we have considered a simplified case of one electron on the t_{1u} molecular level. Applying \vec{H} in a direction $\vec{n} = \vec{H}/H$, where $n_x = \sin \Omega \cos \phi$, $n_y = \sin \Omega \sin \phi$ and $n_z = \cos \Omega$, we find

$$V_{mag} = \vec{H} \vec{L} = H L_{\vec{n}}. \quad (6.9)$$

Here the matrix $L_{\vec{n}}$ is given by

$$L_{\vec{n}} = n_x L_x + n_y L_y + n_z L_z. \quad (6.10)$$

By using Eqs. (2.2a-c) for three t_{1u} MOs, after calculating the matrix elements, we arrive at

$$L_{\vec{n}} = \begin{bmatrix} 0 & -M_0 n_y i & M_0 n_x i \\ M_0 n_y i & 0 & M_0 n_z i \\ -M_0 n_x i & -M_0 n_z i & 0 \end{bmatrix}, \quad (6.11)$$

where $M_0 = 2.5 \mu_B$. The magnetic moments are obtained through the diagonalization of $L_{\vec{n}}$. We find that $\mathcal{M} = 0$ and $\mathcal{M} = \pm 2.5 \mu_B$ for any direction of \vec{H} . The same conclusion is obtained for the case of one h_u -electron (or

h_u – hole). The matrix $L_{\vec{n}}$ then reads

$$L_{\vec{n}} = \begin{bmatrix} 0 & \frac{\sqrt{3}}{2} n_x i & \frac{\sqrt{3}}{2} n_y i & 0 & 0 \\ -\frac{\sqrt{3}}{2} n_x i & 0 & -\frac{1}{2} n_z i & \frac{1}{2} n_y i & -\frac{1}{2} n_x i \\ -\frac{\sqrt{3}}{2} n_y i & \frac{1}{2} n_z i & 0 & \frac{1}{2} n_x i & \frac{1}{2} n_y i \\ 0 & -\frac{1}{2} n_y i & -\frac{1}{2} n_x i & 0 & -n_z i \\ 0 & \frac{1}{2} n_x i & -\frac{1}{2} n_y i & n_z i & 0 \end{bmatrix}. \quad (6.12)$$

The matrix has the same magnetic moments (eigenvalues), which are $0, \pm 1/2, \pm 1$ (in μ_B), for any direction of \vec{H} . The reasoning given above is suggestive and we are looking for a full-scale group-theoretical solution to this problem.

VII. ELECTRON OPTICAL TRANSITIONS

In this section we consider only the electronic dipolar transitions and the corresponding optical lines for C_{60}^{n-} . The picture is not complete because there exist electron-vibration interactions (“Herzberg-Teller” couplings) which can alter the symmetry of the initial or the final state [6]. Here we omit the electron-vibration couplings and limit ourselves to the electronic part of the problem.

The optically active transitions are associated with a nonzero expectation value of the electron dipolar operator \vec{P} . Since the electric-dipole moment,

$$\vec{P} = -e \sum_i \vec{r}_i, \quad (7.1)$$

is an odd quantity in respect to the inversion symmetry, it follows that \vec{P} has no matrix components between states of the same parity. Therefore, all spectral lines due to electric-dipole radiation arise from transitions between states of opposite parity (Laporte’s rule) [13] and the following schemes are relevant for the C_{60}^{2-} and C_{60}^{3-} molecular ions:

$$(t_{1u})^2 \rightarrow t_{1u} t_{1g}, \quad (7.2a)$$

$$(t_{1u})^3 \rightarrow (t_{1u})^2 t_{1g}. \quad (7.2b)$$

These configurations have been considered already in previous sections, and now we can proceed to calculations of optical transitions.

In atoms there are several additional selection rules which greatly facilitate line assignments. These rules are not developed for the icosahedral symmetry and in the following we have to rely on numerical analysis. The total intensity for the line from level A to level B is given by [13]

$$I(A, B) = N(a) \hbar \nu \frac{64\pi^4 \sigma^3}{3h} S(A, B), \quad (7.3)$$

where $N(a)$ is the number of C_{60}^{n-} molecules in state a , $\nu = (E_A - E_B)/h$ is the frequency and $\sigma = h\nu/c$ is the

wave number. Finally, $S(A, B)$ is the line strength which is found as

$$S(A, B) = \sum_{ab} |\langle a | \vec{P} | b \rangle|^2. \quad (7.4)$$

The line strength is a very convenient quantity and in the following we calculate $S(A, B)$ for the transitions (7.2a,b).

The matrix elements of the dipole operator for the case (7.2a) read

$$\langle a | \vec{P} | b \rangle = \sum_{IJ'} \langle a | I \rangle \langle I | \vec{P} | J' \rangle \langle J' | b \rangle, \quad (7.5)$$

where $|I\rangle$ and $|J'\rangle$ are the basis states of $(t_{1u})^2$ and $(t_{1u}t_{1g})$, respectively, while $\langle a | I \rangle$ and $\langle b | J' \rangle$ are the eigenvectors corresponding to levels a and b . The dipole moment (7.1) is a one-electron operator, Sec. III. Its matrix elements are given by

$$\langle I | \vec{P} | J' \rangle = \delta(i_{u1}, j_u) \langle i_{u2} | \vec{P} | j_g \rangle - \langle i_{u1} | \vec{P} | j_g \rangle \delta(i_{u2}, j_u).$$

We recall that $\langle I \rangle = \langle i_{u1}, i_{u2} |$, where i_{u1} and i_{u2} ($i_{u1} > i_{u2}$) are indices referring to six t_{1u} states, and $|J' \rangle = |j_u, j_g \rangle$, Eq. (3.1). From parity consideration it follows that the nonzero matrix elements are of the type $\langle i_u | \vec{P} | j_g \rangle$. In order to calculate them, we first rewrite \vec{P} in the following form:

$$P_x = \sqrt{\frac{4\pi}{3}} r Y_1^{1,c}(\hat{r}), \quad (7.6a)$$

$$P_y = \sqrt{\frac{4\pi}{3}} r Y_1^{1,s}(\hat{r}), \quad (7.6b)$$

$$P_z = \sqrt{\frac{4\pi}{3}} r Y_1^0(\hat{r}). \quad (7.6c)$$

Here Y_1^τ are real spherical harmonics [31], and as before $r = |\vec{r}|$, while \hat{r} stands for the polar angles (Ω, ϕ) . Then we find that the one-electron matrix elements of \vec{P} are

$$\langle i_u | P_k | j_g \rangle = \mathcal{V} c_{1,\tau(k)}(i_u, j_g), \quad (7.7)$$

where $\tau = (1, c)$, $(1, s)$ or 0 for $k = x, y$ and z , respectively. The quantities $c_{l=1,\tau}(i_u, j_g)$ are given by Eq. (3.10) for $l = 1$. In fact, these coefficients have been also used for the calculation of the $(t_{1u}t_{1g})$ and $(t_{1u})^2t_{1g}$ configurations in Sec. IV and V. Finally, the radial part of Eq. (7.7) reads

$$\mathcal{V} = \sqrt{\frac{4\pi}{3}} \int dr r^3 \mathcal{R}_{t1u}(r) \mathcal{R}_{t1g}(r). \quad (7.8)$$

Since we have already computed the eigenvalues and eigenvectors of $(t_{1u})^2$ and $(t_{1u}t_{1g})$ in Sec. V, we now can calculate the line strengths using equations (7.4)-(7.8). The results are quoted in Table XIX.

TABLE XIX: Energies $E_{ab} = \Delta\epsilon_1 + \epsilon_{ab}$ (in eV) and line strengths (in \mathcal{V}) of the transitions $[(t_{1u})^2; a] \rightarrow [(t_{1u}t_{1g}); b]$, $a = 1 - 3$, $b = 1 - 6$, calculated with the model III. Only transitions with $S(a, b) \neq 0$ are given.

	$(t_{1u})^2; a = {}^3T_{1g}$		1H_g		1A_g	
$(t_{1u}t_{1g}); b$	ϵ_{ab}	S	ϵ_{ab}	S	ϵ_{ab}	S
1A_u						
3H_u	-0.350	0.482				
${}^3T_{1u}$	-0.267	0.289				
1H_u			0.392	0.482		
3A_u	0.624	0.386				
${}^1T_{1u}$			0.609	0.161	0.323	0.129

TABLE XX: Energies $E_{ab} = \Delta\epsilon_1 + \epsilon_{ab}$ (in eV) and line strengths (in \mathcal{V}) of the transitions $\{(t_{1u})^3; a\} \rightarrow \{(t_{1u}^2t_{1g}); b\}$, $a = 1 - 3$, $b = 1 - 10$, calculated with the model III. Only the transitions with $S(a, b) \neq 0$ are given.

	$(t_{1u})^3; a = {}^4A_u$		2H_u		${}^2T_{1u}$	
$\{(t_{1u})^2t_{1g}\}; b$	ϵ_{ab}	S	ϵ_{ab}	S	ϵ_{ab}	S
4H_g						
${}^2T_{1g}$			-0.913	0.002	-1.103	$S < 10^{-3}$
1G_g			-0.330	0.450		
${}^2G_u + {}^2T_{2u}$						
${}^4T_{1g}$	-0.010	0.771				
2H_g			-0.158	0.120	-0.349	0.205
${}^2T_{1g}$			0.058	0.072	-0.132	0.120
2H_g			0.508	0.683	0.318	0.277
2A_g					0.589	0.193
${}^2T_{1g}$			0.780	0.602	0.920	0.362

Similarly, one can treat the optical transitions (7.2b) for C_{60}^{3-} . Now we consider the matrix elements of \vec{P} between three-electron basis states $\langle I | (t_{1u})^3 | = \langle i_1, i_2, i_3 |$ and $|J | (t_{1u})^2 t_{1g} \rangle = |j_1, j_2, j_g \rangle$, and obtain

$$\begin{aligned} \langle I | \vec{P} | J \rangle = & \langle i_1 | \vec{P} | j_g \rangle \delta(i_2, j_1) \delta(i_3, j_2) - \langle i_1 | \vec{P} | j_g \rangle \delta(i_2, j_2) \delta(i_3, j_1) \\ & + \langle i_2 | \vec{P} | j_g \rangle \delta(i_1, j_2) \delta(i_3, j_1) - \langle i_2 | \vec{P} | j_g \rangle \delta(i_1, j_1) \delta(i_3, j_2) \\ & + \langle i_3 | \vec{P} | j_g \rangle \delta(i_1, j_1) \delta(i_2, j_2) - \langle i_3 | \vec{P} | j_g \rangle \delta(i_1, j_2) \delta(i_2, j_1). \end{aligned}$$

Here again, the one-electron matrix elements $\langle i_u | \vec{P} | j_g \rangle$ are specified by Eq. (7.7). The resulting line strengths are quoted in Table XX.

It follows from Table XIX that for C_{60}^{2-} there are three lines from the ground state ${}^3T_{1g}$,

$$E({}^3T_{1g} \rightarrow {}^3H_u) = \Delta\epsilon_1 - 0.350 \text{ eV}, \quad (7.9a)$$

$$E({}^3T_{1g} \rightarrow {}^3T_{1u}) = \Delta\epsilon_1 - 0.267 \text{ eV}, \quad (7.9b)$$

$$E({}^3T_{1g} \rightarrow {}^3A_u) = \Delta\epsilon_1 + 0.624 \text{ eV}. \quad (7.9c)$$

With $\Delta\epsilon_1 = 1.153$ eV, Eq. (5.5), we obtain $E({}^3T_{1g} \rightarrow {}^3H_u) = 0.803$ eV, $E({}^3T_{1g} \rightarrow {}^3T_{1u}) = 0.886$ eV and $E({}^3T_{1g} \rightarrow {}^3A_u) = 1.777$ eV. These values should be compared with two dominant bands at 1.305 eV (950 nm)

and 1.494 eV (830 nm) observed by the near-infrared experiments in solutions [9]. We conclude that first two transitions can be tentatively ascribed to the experimental bands if $\Delta\epsilon_1$ is taken to be larger, $\Delta\epsilon_1 \sim 1.7$ eV. Here it is worth to notice that in our approach $\Delta\epsilon_1$ in Eq. (5.5) remains a phenomenological quantity which is not immediately connected with the term splittings. In Ref. 16 the authors have obtained that the ground state of C_{60}^{2-} is the 1A_g singlet. We have shown in Sec. V that this is possible if $\Delta\epsilon_1$ is small, see Fig. 3. However, if 1A_g is the ground state, then there is only one optical transition ($^1A_g \rightarrow ^1T_{1u}$ at $\Delta\epsilon_1 + 0.323$ eV, Table XIX) and comparison with the experiment becomes even more problematic. We conclude that our calculations are basically in agreement with the experiment for C_{60}^{2-} , although also a third band is expected. The position of the third band however can change due to the effect of configuration mixing discussed in Sec. V.

The situation is less clear for the C_{60}^{3-} molecular ion. Both our calculations and those of Ref. 16 predict that the ground state is the 4A_u level. Then from Table XX we find that the only optical transition allowed by the selection rules is $^4A_u \rightarrow ^4T_{1g}$. This is at variance with the experimental consensus for three dominant bands at 1350, 960 and 770 nm [9]. In principle, the theoretical line $^4A_u \rightarrow ^4T_{1g}$ can be split by the crystal field and Jahn-Teller distortions, but the magnitude of the splitting (~ 0.3 eV) seems excessive. The other possibility is if some transitions become allowed through the “Herzberg-Teller” (electron-vibration) mechanism [6]. Further experimental and theoretical investigations are needed to clarify the issue.

VIII. DISCUSSION AND CONCLUSIONS

We have presented an efficient configuration interaction method for many electron (hole) molecular terms of the $C_{60}^{m\pm}$ molecular ion. The method is based on the multipole expansion of the Coulomb interactions and takes into account the molecular symmetry. Although there are some similarities with approaches used for treating many electron effects in atomic calculations [39], the technique is novel and original. Crystal electric field effects [14] and the spin-orbit coupling can be easily incorporated in the calculation. The technique can be used for other electron systems.

We have applied the method for studying molecular terms of electron and hole configurations of $C_{60}^{n-/m+}$ ($n = 2-4$, $m = 2-5$), and for excitonic configurations ($h_u^+ t_{1u}^-$) and ($h_u^+ t_{1g}^-$) of the neutral molecule. In most of the cases the ground state is found to obey Hund’s rules.

Our calculations of the molecular term structure (t_{1u}) 2 for C_{60}^{2-} differs from the previous result of Negri *et al.*, Ref. 16. They have reported that the ground term of C_{60}^{2-} is the 1A_g singlet, while we have found that for realistic parameters ($\Delta\epsilon_1 = 1.15$ eV [9, 38]) it is the $^3T_{1g}$ triplet, in accordance with Hund’s rules. We have shown (Fig. 3

and Sec. V) that the reason for this is that in Ref. 16 the one-electron energy difference between t_{1g} and t_{1u} states is too small, $\Delta\epsilon_1 = 0.64$ eV.

Our results for the $(h_u^+)^2$ hole configuration indicate that there are three very close (~ 0.03 eV) low lying molecular triplets of $^3T_{1g}$, 3G_g and $^3T_{2g}$ symmetry. The lowest molecular terms for $(h_u^+)^3$ belong to the $^4T_{1u}$, 4G_u and $^4T_{2u}$ symmetry. The number of states in a small energy interval $\Delta\epsilon \sim 0.03$ eV near the ground state is 30, 40, 25, 6 for hole configurations $(h_u^+)^m$ with $m = 2, 3, 4, 5$, respectively. This suggests that the configuration of $m = 3$ holes is most susceptible for Jahn-Teller distortions of the C_{60} molecule and possibly for hole-phonon coupling which causes superconductivity [2].

We have calculated the magnetic moments of the $(t_{1u})^n$ and $(h_u^+)^m$ configurations, Sec. VI. The coupling of spin and orbital momenta differs from the Landé g -factor scheme of atoms. The magnetic moments do not depend on the orientation of the molecule with respect to an external magnetic field. The latter statement was demonstrated explicitly for the case of one t_{1u} electron and one h_u hole. We consider this as a group-theoretical puzzle of the icosahedral symmetry. We have also found new “accidental” degeneracy between the 2G_g and $^2T_{2g}$ states of the $(t_{1u})^2 t_{1g}$ and $(t_{1g})^2 t_{1u}$ configurations (Tables VII and XIV.)

Finally, we have studied optical absorption associated with electron dipolar transitions $(t_{1u})^2 \rightarrow (t_{1u} t_{1g})$ and $(t_{1u})^3 \rightarrow (t_{1u})^2 t_{1g}$. For C_{60}^{2-} we have found that two lines ($^3T_{1g} \rightarrow ^3H_u$ and $^3T_{1g} \rightarrow ^3T_{1u}$) can be tentatively ascribed to the two near-infrared dominant bands at 950 and 830 nm. However, in addition a third band ($^3T_{1g} \rightarrow ^3A_u$) is expected from the calculation. For C_{60}^{3-} with 4A_u as the ground state, we have found that only one electron dipolar transition, $^4A_u \rightarrow ^4T_{1g}$, is allowed. It seems that a better understanding of optical transitions requires a study of the Herzberg-Teller (electron-vibration) effect which is beyond the scope of the present work. We suggest to perform optical experiments for C_{60}^{n-} and C_{60}^{m+} in the gas phase to obtain more precise and full data on the optical lines which can shed light on the problem of electronic intra-molecular correlations.

Acknowledgments

We thank M. Lueders, N. Manini, E. Tosatti, and F. Negri for interesting discussions, P. Launois, A. Ceulemans and P.N. Dyachkov for informing us about useful references. This work has been financially supported by the Fonds voor Wetenschappelijk Onderzoek, Vlaanderen.

APPENDIX A: L_z FOR A ROTATED MOLECULE

If the molecule is rotated away, then the MOs of t_{1u} and h_u symmetry are given by Eqs. (2.2a-c) and (2.1a-

e) in the coordinate system (x', y', z') attached to the molecule. The rotated functions can be expanded in terms of real spherical harmonics (RSH) defined in the fixed set of axes (x, y, z) . For example, a rotation R defined by three Euler angles $\omega = (\alpha, \beta, \gamma)$ transforms $\psi_1(t_{1u})$ to

$$\begin{aligned}\psi'_1(t_{1u}) &= R(\omega) \psi_1(t_{1u}) \\ &= \frac{6}{\sqrt{50}} R(\omega) Y_5^0 + \sqrt{\frac{7}{25}} R(\omega) Y_5^{5,c}.\end{aligned}\quad (\text{A1})$$

Here $R(\omega) Y_5^0$ and $R(\omega) Y_5^{5,c}$ defines the rotations of Y_5^0 and $Y_5^{5,c}$, respectively. The rotated functions can be found from Eqs. (B5), and (B9), quoted in the Appendix B. Analogously, we proceed with the other angular functions of t_{1u} and h_u symmetry. In general,

$$R(\omega) Y_l^\tau = \sum_{\tau'} Y_l^{\tau'} U_{\tau' \tau}^l(\omega). \quad (\text{A2})$$

Here $\tau, \tau' = (m, c)$, (m, s) or 0, and the rotator functions (matrices) $U_{\tau' \tau}^l(\omega)$ are specified in Appendix B, Eqs. (B5), (B7), and (B9). Now we are ready to calculate $L_z \psi'_k(t_{1u})$ ($k = 1 - 3$) and $L_z \psi'_k(h_u)$ ($k = 1 - 5$). By means of Eq. (6.4) we obtain

$$\begin{aligned}\langle k | L_z | k' \rangle|_\omega &= i \sum_{m>0} m (g_{(m,s)k} g_{(m,c)k'} - g_{(m,c)k} g_{(m,s)k'}),\end{aligned}\quad (\text{A3})$$

where the functions $g_{\tau,k}$ depend on ω ,

$$\begin{aligned}g_{(m,c)k}(\omega) &= \alpha(\tau_1) U_{(m,c)\tau_1}^l(\omega) + \alpha(\tau_2) U_{(m,c)\tau_2}^l(\omega), \\ g_{(m,s)k}(\omega) &= \alpha(\tau_1) U_{(m,s)\tau_1}^l(\omega) + \alpha(\tau_2) U_{(m,s)\tau_2}^l(\omega).\end{aligned}$$

Here $\alpha(\tau)$ stands for the coefficients of expansion of MOs of t_{1u} and h_u symmetry in terms of RSH,

$$\psi_k(\Omega) = \alpha(\tau_1) Y_l^{\tau_1}(\Omega) + \alpha(\tau_2) Y_l^{\tau_2}(\Omega), \quad (\text{A5})$$

see Eqs. (2.2a-c) and (2.1a-e). For example, for the first MO ($k = 1$) of t_{1u} symmetry we have $\tau_1 = 0$, $\alpha(\tau_1) = 6/\sqrt{50}$ and $\tau_2 = (5, c)$, $\alpha(\tau_2) = \sqrt{7/25}$, and etc. The indices k, k' in (A3) belong to the same molecular shell (t_{1u} or h_u), otherwise $\langle k | L_z | k' \rangle|_\omega = 0$. From Eq. (A3) we also conclude that

$$\langle k | L_z | k \rangle|_\omega = 0, \quad (\text{A6a})$$

$$\langle k | L_z | k' \rangle|_\omega = \langle k' | L_z | k \rangle|_\omega^*. \quad (\text{A6b})$$

The former condition is a consequence of working with real spherical harmonics, the latter ensures the hermiticity of L_z .

APPENDIX B: ROTATION OF REAL SPHERICAL HARMONICS

An active rotation R is specified by its Euler angles $\omega = (\alpha, \beta, \gamma)$ [31]. It transforms a complex spherical harmonic Y_l^m to $Y'_l{}^m$, where

$$Y'_l{}^m = R(\omega) Y_l^m = \sum_n Y_l^n D_{nm}^l(\omega). \quad (\text{B1a})$$

For $Y'_l{}^{-m}$ we have

$$Y'_l{}^{-m} = R(\omega) Y_l^{-m} = \sum_n Y_l^n D_{n-m}^l(\omega). \quad (\text{B1b})$$

Here D_{nm}^l stands for the Wigner functions given by

$$D_{nm}^l(\alpha, \beta, \gamma) = C_{nm} e^{-in\gamma} d^l(\beta)_{nm} e^{-im\alpha}. \quad (\text{B2})$$

$d^l(\beta)_{nm}$ is a reduced matrix element which is a real quantity, and $C_{nm} = \pm 1$ depending on n, m (see Eqs. (2.1.6) and (2.1.5) of Refs. 31). From Eq. (B2) and the properties

$$d(\beta)_{-n, -m} = (-1)^{n+m} d(\beta)_{nm}, \quad (\text{B3a})$$

$$C_{-n, -m} = (-1)^{n+m} C_{nm} = (-1)^{n+m} C_{nm}^*, \quad (\text{B3b})$$

we find that

$$D_{-n-m}^l(\omega) = D_{nm}^l(\omega)^*. \quad (\text{B4})$$

We then combine (B1a) with (B1b) and use Eq. (B4) for deriving the transformation law of real spherical harmonics. After some algebra we find

$$\begin{aligned}R Y_l^{m,c} &= Y_l^0 U_{0;(m,c)}^l \\ &+ \sum_{n>0} \left(Y_l^{n,c} U_{(n,c);(m,c)}^l + Y_l^{n,s} U_{(n,s);(m,c)}^l \right),\end{aligned}\quad (\text{B5})$$

where $U_{0;(m,c)}^l = \sqrt{2} \operatorname{Re} D_{0m}^l$, and

$$U_{(n,c);(m,c)}^l = \operatorname{Re}(D_{nm}^l + D_{n-m}^l), \quad (\text{B6a})$$

$$U_{(n,s);(m,c)}^l = -\operatorname{Im}(D_{nm}^l + D_{n-m}^l). \quad (\text{B6b})$$

In Eqs. (B5)-(B6b) and below for clarity we drop the argument ω . Analogously, rotating $Y_l^{m,s}$ we obtain

$$\begin{aligned}R Y_l^{m,s} &= Y_l^0 U_{0;(m,s)}^l \\ &+ \sum_{n>0} \left(Y_l^{n,c} U_{(n,c);(m,s)}^l + Y_l^{n,s} U_{(n,s);(m,s)}^l \right),\end{aligned}\quad (\text{B7})$$

where $U_{0;(m,s)}^l = \sqrt{2} \operatorname{Im} D_{0m}^l$, and

$$U_{(n,c);(m,s)}^l = \operatorname{Im}(D_{nm}^l - D_{n-m}^l), \quad (\text{B8a})$$

$$U_{(n,s);(m,s)}^l = \operatorname{Re}(D_{nm}^l - D_{n-m}^l). \quad (\text{B8b})$$

Finally, the rotation of Y_l^0 yields

$$R Y_l^0 = Y_l^0 U_{0;0}^l + \sum_{n>0} \left(Y_l^{n,c} U_{(n,c);0}^l + Y_l^{n,s} U_{(n,s);0}^l \right), \quad (\text{B9})$$

where $U_{0;0}^l = D_{00}^l$, $U_{(n,c);0}^l = \sqrt{2} \operatorname{Re} D_{n0}^l$ and $U_{(n,s);0}^l = -\sqrt{2} \operatorname{Im} D_{n0}^l$.

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